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## Combined experimental and computational investigations of the fluorosolvatochromism of chromeno[4,3-b]pyridine derivatives: Effect of the methoxy substitution

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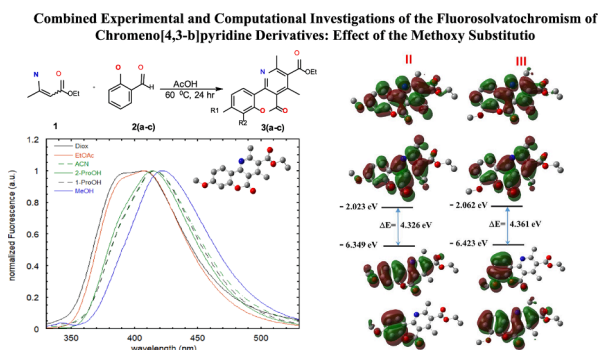
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### HIGHLIGHTS

- The position of the substitution of the methoxy substituent on the chromeno moiety is crucial for yielding fluorescent derivatives.
- The 7-methoxy-chromeno[4,3-b]pyridine-3-carboxylate derivative is found to be highly fluorescent compared with the 8-methoxy analogue.
- The notable fluorescence properties of the 7-methoxy derivative are rationalized in accordance with potential ICT.
- The 7-methoxy derivative exhibited a positive fluorosolvatochromic behavior in neat solvents.
- The spectral properties and corresponding fluorosolvatochromism of the 7-methoxy derivative are rationalized employing the DFT/ TD-DFT methods.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

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### ABSTRACT

Extensive research has been conducted on the spectral properties of chromeno[4,3-b]pyridine derivatives, owing to their potential applications in sensing, optoelectronic devices, and drug discovery. This study presents a comprehensive investigation into the fluorosolvatochromism of selected chromeno[4,3-b]pyridine derivatives, with a particular emphasis on the impact of methoxy substitution. Three derivatives were synthesized and subjected to spectral analysis: chromeno[4,3-b]pyridine-3-carboxylate (I) as the parent compound, and its 7-methoxy (II) and 8-methoxy (III) substituted derivatives. The UV-Vis absorption spectra of all derivatives exhibited a broad band with a maximum absorption wavelength that remained unaffected by the surrounding medium. However, distinct fluorescence properties were observed among them. Specifically, derivative II displayed notable fluorescence, while derivatives I and III exhibited no fluorescence properties. Furthermore,

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derivative II exhibited a fluorescence spectrum that is significantly influenced by the polarity of the medium. To investigate the fluorosolvatochromic behavior in depth, we conducted a comprehensive analysis using various neat solvents with different polarities and hydrogen bonding capabilities. The results obtained revealed a significant positive fluorosolvatochromism, with a bathochromic shift in the fluorescence spectrum as the solvent polarity increased. To understand how specific and non-specific interactions between the solute and the solvent affected the fluorosolvatochromism of II, we employed the four empirical scales model of Catalán. The obtained results demonstrated that intramolecular charge transfer played a crucial role in the fluorescence behavior of II. To provide a molecular-level explanation for the experimental spectral properties, we utilized the DFT and TD-DFT/B3LYP/6-31 + G(d) computational methods with the IEFPCM implicit solvation approach. The spectral differences between II and III were rationalized in terms of the frontier molecular orbitals (FMOs: the HOMO and LUMO), where distinct natures were observed among the examined derivatives. This study offers valuable insights into the impact of methoxy substitution on the physical and chemical properties of chromeno[4,3-b]pyridine derivatives, specifically concerning their spectral properties as elucidated by their fluorosolvatochromic behavior.

## 1. Introduction

Coumarin serves as a ubiquitous structural framework, forming the core of numerous naturally occurring and synthetic molecules employed in a wide range of applications [1–3]. The diverse applications of coumarin-containing compounds underscore the ongoing extensive research aimed at discovering new synthetic methods to access coumarins with a variety of substitution patterns [4–10], the study of coumarin photochemical and photophysical properties, and exploring their utilization in various applications [11–15]. Coumarin-based molecules exhibit a wide spectrum of pharmaceutical activities, including antibacterial [16], antifungal [17], antiviral [18], anti-inflammatory [19], antitumor [20], anticancer [21], antidiabetic [22], antihypertensive [23], and Antineurodegenerative activities [24]. With its pharmaceutical activities, coumarin is found in various marketed drugs, including the anticoagulant agent warfarin [25]. Moreover, coumarin framework is embedded in the structures of many insecticides [26], and food additives [27]. Furthermore, due to their high fluorescent quantum yield, long decay times, large Stokes shifts, and response to their microenvironments [28–30], coumarins generally exhibit a variety of interesting photophysical properties that enable them to be utilized in the design and synthesis of fluorescence sensors [31], fluorescence dyes [32,33], laser dyes [34,35], and optical devices [7,36,37].

Substituted coumarins, particularly 7- and 8-methoxy-coumarins, have garnered significant attention from medicinal and material

chemists. This interest stems from reports indicating that the presence of a methoxy group on the coumarin skeleton enhances their biological activities [38], and affects the photophysical and photochemical properties of substituted coumarins [39,40]. For example, isofraxidin (A), Fig. 1, has shown activity against lung cancer cells [41], naturally occurring polyneomarine C (B) is used in Chinese herbal medicine [42], Scopolamine (C) is an immunosuppressant [43], the methoxy coumarin D is an active antifungal agent [44] and coumarin F is an anticancer agent [45]. Furthermore, methoxy-substituted triazolyl coumarin E as a  $\text{Hg}^{2+}$  selective fluorescent chemosensors [46], and compound G is a  $\text{Zn}^{2+}$  fluorescent chemosensor [47]. In addition to the substitution on the coumarin core, heterocycles fused to the lactone ring of the coumarins result in a synergistic effect of both the coumarin and the heterocycle [5,48–52]. Moreover, pyridocoumarins are a privileged class of heterocycle-fused coumarins that are spread in natural products and in compounds employed for versatile applications [50,51,53].

Importantly, in order to obtain a comprehensive understanding of the behavior of these intriguing coumarins, spectral studies offer crucial insights into their physicochemical properties [54–56]. The data obtained from spectral studies are essential for comprehending and interpreting charge distribution, identifying nucleophilic and electrophilic sites during potential chemical reactions, assessing solvent polarity, and most importantly, understanding the changes in electronic distribution and geometric structure upon excitation [57,58]. Therefore, solvatochromism is a widely employed technique for investigating these

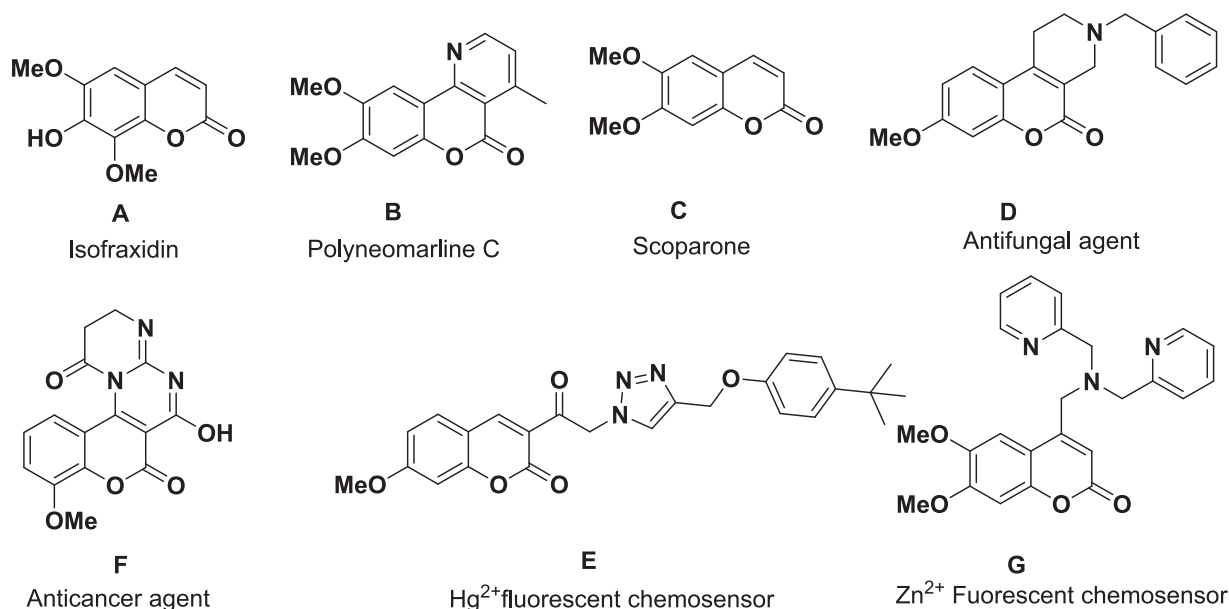


Fig. 1. Methoxy coumarins utilized in different applications.

aspects of molecules, both in their ground state and upon excitation [59]. This exciting phenomenon involves analyzing the electronic spectra of potential probes in various solvents with different polarities and hydrogen bond donor/acceptor properties [54,57,59], where the solvent-molecule interaction is observed mainly through a change in the shape and intensity of the electronic spectral bands [60–62].

In this study, we investigated the impact of the surrounding medium on the physicochemical and spectral properties of three chromeno[4,3-b]pyridine derivatives: the parent compound (I) without methoxy substitution, and derivatives (II) and (III) with 7- and 8-methoxy substitutions, respectively. The chemical structures of all derivatives are displayed in Fig. 2. Furthermore, we rationalized the associated fluorosolvatochromism by employing the linear solvation model of Catlán. To gain insights into the structural effects of the methoxy substituent on the fluorosolvatochromic behaviors of the examined derivatives, as well as to provide molecular-level interpretation related to the corresponding structural effects, we utilized DFT and TD-DFT approaches.

## 2. Experimental

### 2.1. Materials

Solvents were supplied by Sigma-Aldrich, and used without further purification. All organic solvents were of spectroscopic grades and used as received.

### 2.2. Synthesis

The substituted chromeno[4,3-b]pyridine-3-carboxylates **3(a-c)** were synthesized according to a reported procedure [63]; more details are provided in the [supplementary materials](#).

### 2.3. Procedures and spectroscopic measurements

Stock solutions ( $3.0 \times 10^{-4}$  M) were prepared for each compound in methanol. The working solution of approximately  $3.0 \times 10^{-6}$  M was prepared through the process of first removing an aliquot of the stock solution that had been created using methanol, and then evaporation at room temperature and ambient pressure. After that, the residue was redissolved in the relevant volume of the solvent of interest. The UV–Vis absorption and fluorescence spectra of the synthesized compounds were measured in neat solvents and ultrapure deionized water using Agilent double beam spectrophotometer in quartz cells. The fluorescence quantum yield was calculated as described previously [56].

### 2.4. Computational methods

All DFT and TD-DFT calculations were performed with *Gaussian 09*

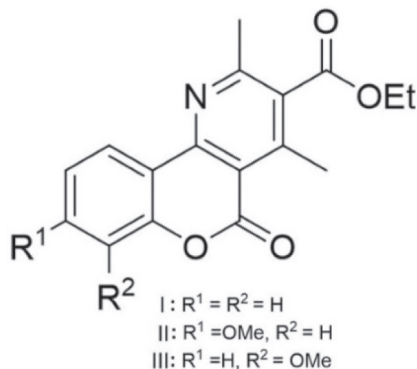


Fig. 2. Chemical structures of chromeno[4,3-b]pyridine-3-carboxylates derivatives investigated in the current study.

version D.01. The hybrid B3LYP functional and the 6-31 + G(d) basis set were utilized in order to carry out the whole molecular geometry optimization [64]. The implicit solvent effect was considered employing the integral equation formalism polarizable continuum model (IEFPCM) [65]. The time-dependent version of DFT, namely TD-DFT, with B3LYP functional and 6-31 + G(d) basis set were utilized to simulate the absorption and emission spectra. Using the optimized ground-state geometry as an input geometry, the simulated absorption spectra were computed for the first eighteen excitation states. The multilinear regression analysis, also known as MLRA, was carried out using Excel in its default configuration.

## 3. Results and discussion

### 3.1. The absorption and emission spectra

The absorption spectra of all three derivatives of chromeno[4,3-b]pyridine, namely I, II, and III, were initially measured in methanol. The UV–Vis absorption spectra of all three derivatives displayed a broad band with a maximum absorption wavelength that remained unchanged regardless of the surrounding medium. Additionally, we attempted to measure the fluorescence spectra of all derivatives in various media and at different concentrations. However, II exhibited remarkable fluorescence properties, whereas I and III showed no fluorescence, classifying them as non-fluorescent molecules. Therefore, the parent compound was excluded from further analysis, and all subsequent comparative analyses were focused on II versus III. Fig. 3 displays the normalized absorption spectra of II and III, along with the normalized fluorescence spectrum of II. By examining the absorption spectra shown in Fig. 3, it can be observed that II and III have  $\lambda_{\max}$  values of 310 nm and 280 nm, respectively. This shift in  $\lambda_{\max}$  can be attributed to the position of the methoxy substituent, indicating distinct intramolecular structural effects. However, it is important to note that the results obtained from the absorption spectroscopy method revealed minimal dependency on solvent effects. Consequently, we conducted a comprehensive investigation into the solvatochromism of II using steady-state fluorescence spectroscopy in a variety of solvents with varying polarity and hydrogen bonding capabilities.

**Fluorosolvatochromic behavior of II.** The influence of solvents on the fluorescence spectra of II was investigated using a range of neat solvents with varying polarities and hydrogen bonding capabilities. The parameters of the solvents, along with the spectral properties of II, are compiled in Table 1. The selected solvents are categorized into three

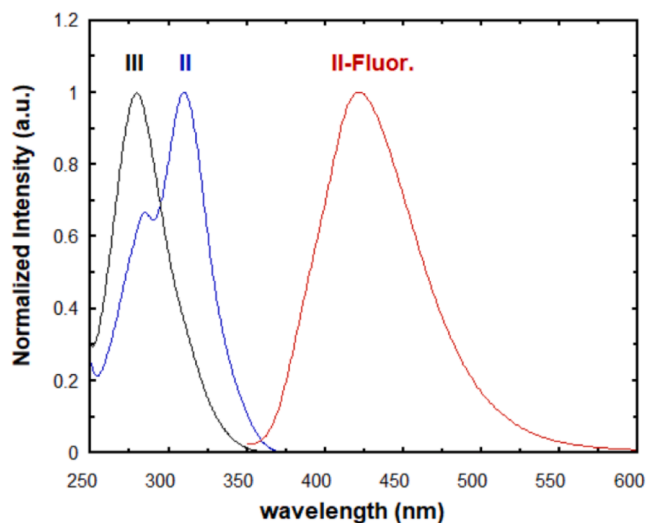


Fig. 3. Absorption spectra of II and III and fluorescence spectrum of II in methanol.

**Table 1**

Solvent parameters and spectral properties of II.

Solvent	$\Delta f$	SP	SdP	SA	SB	$\lambda_{\text{abs}}$ (nm)	$\lambda_{\text{Fluo}}$ (nm)	$\Delta\nu$ (cm <sup>-1</sup> )	Fluor. QY
<i>Polar protic</i>									
Water	0.320	0.681	0.997	1.062	0.025	310	444	9736	0.120
Methanol	0.31	0.608	0.904	0.605	0.545	310	422	8561	0.109
Ethanol	0.289	0.633	0.783	0.400	0.658	310	419	8392	0.108
1-Butanol	0.264	0.674	0.655	0.341	0.809	311	415	8058	0.061
2-Butanol	0.262	0.656	0.706	0.221	0.888	310	412	7986	0.034
1-Propanol	0.274	0.658	0.748	0.367	0.782	311	416	8116	0.110
Isopropanol	0.276	0.633	0.808	0.283	0.83	310	414	8103	0.141
<i>Polar aprotic</i>									
Ethylacetate	0.200	0.656	0.603	0	0.542	311	408	7645	0.018
DCM	0.218	0.761	0.769	0.040	0.178	311	406	7524	0.035
DMF	0.276	0.759	0.977	0.031	0.613	313	420	8139	0.148
Acetonitrile	0.305	0.645	0.974	0.044	0.286	310	415	8162	0.081
DMSO	0.264	0.83	1.000	0.072	0.647	313	424	8364	0.085
<i>Non-polar</i>									
1,4-Dioxane	0.020	0.737	0.312	0	0.444	312	405	7360	0.034
Chloroform	0.153	0.783	0.614	0.047	0.071	311	389	6447	0.052
Cyclohexane	0.005	0.683	0	0	0.073	312	374	5313	0.003
Hexane	0.001	0.616	0	0	0.056	312	376	5456	0.002

groups: polar protic, polar aprotic, and nonpolar, as indicated in Table 1. The measured fluorescence spectra of II in these selected solvents, normalized to unity with respect to  $\lambda_{\text{max}}$ , are depicted in Fig. 4. From Fig. 4, it is evident that as the polarity of the solvents increased, a significant bathochromic shift was observed, indicating a positive fluorosolvatochromic behavior for II. This behavior caused a shift of up to 70 nm across the range of examined solvents, as noted in Table 1. Furthermore, the fluorescence spectrum displayed more vibronic fine structure in nonpolar solvents compared to their polar counterparts. The first emission peak, appearing as a shoulder at a shorter wavelength than the second emission peak, gradually disappeared as the solvent polarity increased.

In principle, when molecules exhibit UV-Vis absorption unaffected by the polarity of the surrounding medium but display solvatochromic behavior in their fluorescence spectra (a red shift with increasing polarity), it typically indicates the presence of photo-induced intramolecular charge transfer (ICT) in the singlet excited state. This phenomenon is commonly observed in compounds with a conjugated  $\pi$ -electron system, where electron donor and acceptor groups are present across the backbone of the molecule [66,67]. Accordingly, an ICT is

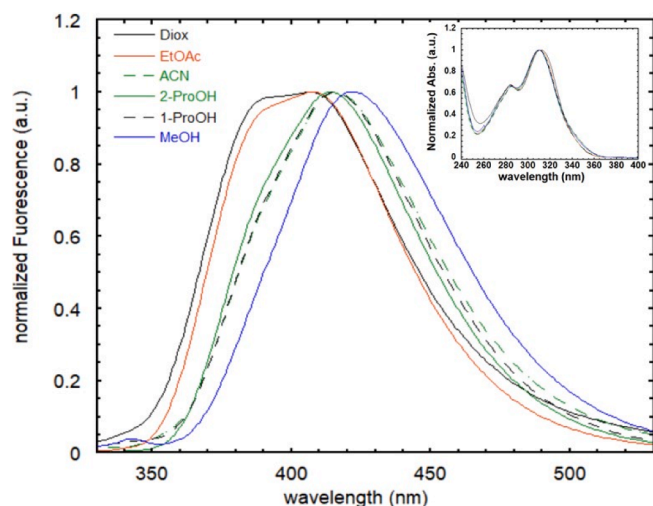
proposed for II, as displayed in Scheme 1. Hence, it can be hypothesized that the ICT yields a zwitterionic form of II with charge separation that is more stabilized by a polar solvent.

Moreover, generally, a notable shift in the fluorescence spectrum of a molecule can be attributed to specific and nonspecific interactions with the solvent molecules under the influence of solvation. Thus, in order to rationalize the effects of various solvent parameters on the fluorescence spectra of II, we employed the four empirical scales model of Catalán. It is noteworthy to mention that this model is more detailed compared with the typical Kamlet-Taft analogue, where the dipolarity/polarizability parameter ( $\pi^*$ ) is split into two parameters, namely solvent polarizability (SP) and dipolarity (SdP) [68,69]. The Catalán model defines the solvent-dependent physicochemical property (A) compared to counterpart value in the gas phase ( $A_0$ ) according to the following equation:

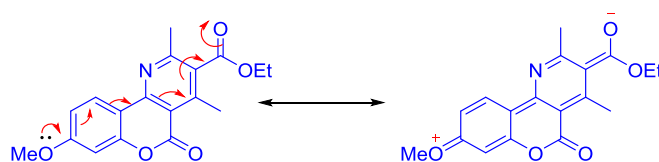
$$A = A_0 + bSA + cSB + dSP + eSdP \quad (1)$$

where b, c, d, and e are the regression coefficients of the empirical solvent parameters of acidity (SA), basicity (SB), dipolarity (SdP), and polarizability (SP), respectively. The magnitude of these regression constants refers to the sensitivity of the physicochemical properties to a corresponding solvent-solute interaction. The MLRA was applied to three spectral properties of II employing the Catalán model, namely fluorescence maximum wavelength ( $\lambda_{\text{Fluo}}$ ), Stokes shift ( $\Delta\nu$ ), and Fluorescence Quantum Yield (FQY). The following equations were concluded:

$$\begin{aligned} \lambda_{\text{Fluo}} &= (357 \pm 22) + (29 \pm 32)SA + (32 \pm 7)SB + (27 \pm 8)SP + (11 \pm 6)SdP \quad R \\ &= 0.950 \end{aligned} \quad (2)$$



**Fig. 4.** Fluorescence spectra of compounds II in selected neat solvents ( $\lambda_{\text{ex}} = 310$  nm); inset: normalized absorption spectra.



**Scheme 1.** Proposed resonance structures of II.



$$\begin{aligned}\Delta\nu &= (5211 \pm 1276) + (472 \pm 1862)SA + (2211 \pm 342)SB + (1579 \\ &\quad \pm 452)SP + (704 \pm 375)SdP \quad R \\ &= 0.958\end{aligned}\quad (3)$$

$$\begin{aligned}FQY &= (0.002 \pm 0.109) - (0.018 \pm 0.032)SA + (0.090 \pm 0.037)SB \\ &\quad + (0.042 \pm 0.039)SP + (0.024 \pm 0.032)SdP \quad R \\ &= 0.815\end{aligned}\quad (4)$$

As can be seen from Eq. (1), an equal contribution of around 30% is found from SA, Sb, and SP. This finding is suggestive of contributions coming from both specific and nonspecific solute-solvent interactions. In addition, each of the solvent parameters was shown to have a significant influence on the induction of a bathochromic shift into  $\lambda_{Fluo}$ . However, a more dominant effect for SB (45%) and SP (32%), and much lower effects for SA and SdP, are observed. Yet, positive contributions on  $\Delta\nu$  is observed for all parameters. For the FQY, the SB, SP, and SdP exhibited positive contributions of similar levels compared to  $\Delta\nu$ , whereas negative contributions were observed for the SA, indicative of potential quenching of the fluorescence intensity. Based on these findings, it is hypothesized that dipole-dipole interactions and hydrogen bonding (HB) can result in ionic coupling and solvation within the molecular environment of II, thereby influencing the corresponding fluorosolvatochromic behavior. Furthermore, per the acceptable correlation coefficient (R) value obtained for the MLRA, the acquired modules were employed to potentially predict the spectral properties of II using the same tested solvents. Fig. 5 displays the correlation between the measured and predicted spectral properties in all tested solvents. As can be noted, good correlation coefficients were obtained for  $\lambda_{Fluo}$  (R: 0.95) and  $\Delta\nu$  (R: 0.96), whereas reasonable correlation was obtained for FQY (R: 0.81). In addition, upon applying eq. (4), one can notice that the examined solvent exhibit two distinctive behaviors in reference to the experimental spectral properties compared to the predicted value, namely positive and negative deviations. Nonetheless, the majority of the solvents exhibited minimal deviation for  $\lambda_{Fluo}$  and  $\Delta\nu$  with R values of 0.95 and 0.96, respectively. These findings indicate reasonable validity for the employed approach. However, in order to rationalize the solvent effect on the spectral properties of II, further analysis employing specific computational chemistry techniques is required.

Based on the positive fluorosolvatochromic behavior observed for II, further solvatochromic assessment was attempted employing the Lippert-Mataga approach. In this model, the  $\Delta\nu$  is correlated to the effect of solvent polarizability ( $\Delta f$ ) according to the following equation:

$$\Delta\nu = \frac{2(\mu_{ex} - \mu_g)^2}{hca^3} \Delta f + const. \quad (5)$$

where  $\mu_{ex}$  and  $\mu_g$  are the dipole moments of the molecule in its excited and ground states, respectively;  $h$ : Planck's constant;  $a$ : the cavity radius in which the fluorophore resides;  $c$ : speed of light. The change in  $\mu$  ( $\Delta\mu = \mu_{ex} - \mu_g$ ) can be calculated from the slope  $\left(\frac{2(\mu_{ex} - \mu_g)^2}{hca^3}\right)$  of the linear plot of  $\Delta\nu$  vs.  $\Delta f$ . A value of 4.2 Å was estimated for the cavity radius employing the DFT- optimized geometry of II. The Lippert-Mataga plots for the polar protic and polar aprotic sets of solvents were constructed as illustrated in Fig. 6. As can be noted, positive slopes were obtained for both categories of solvents, indicative of a positive value for the  $\Delta\mu$  upon excitation, which in turn indicates a higher value for  $\mu_e$  compared to  $\mu_g$ . Indeed, these findings are in good agreement with the positive fluorosolvatochromic behavior of II. Consequently, we attempted to calculate  $\Delta\mu$  upon excitation for both the locally excited (LE) and ICT states. Our calculations revealed  $\Delta\mu$  values of 2.43 and 4.21 D for the LE and ICT states, respectively. These values indicate a partial separation of charges that is consistent with the proposed ICT displayed in Scheme 1.

**DFT, TD-DFT, and molecular orbitals characteristics.** The optimization

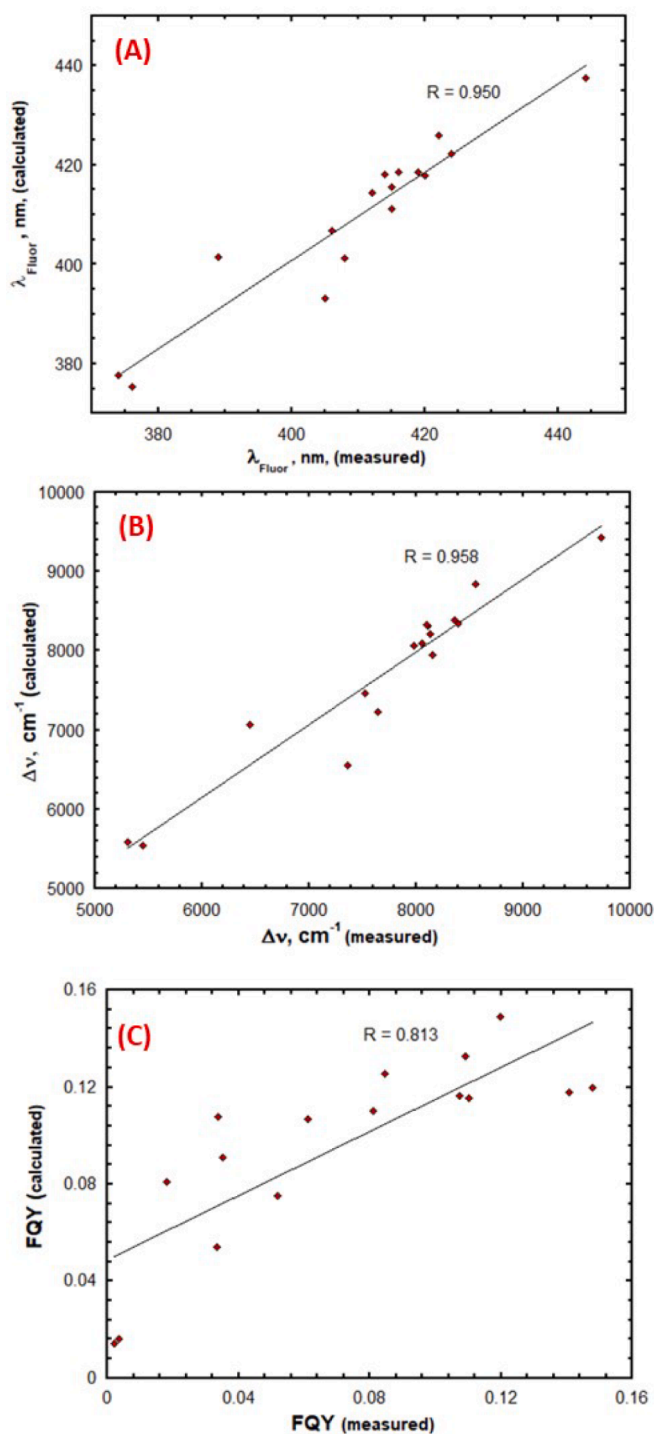


Fig. 5. Correlation between predicted and measured spectral properties of II; (A)  $\lambda_{Fluo}$ , (B)  $\Delta\nu$ , (C) FQY.

of the molecules under investigation is crucial for conducting other computational experiments, such as simulating the UV-Vis absorption spectra in the relevant medium. Fig. 7 displays the optimized geometry of II in both the ground and excited states, using DFT (B3LYP/6-31G+(d), IEFPICM, methanol). One key difference between the ground and excited state geometries can be observed for the O-C bond that links the methoxy group with the ring (indicated by arrows in Fig. 7). The DFT calculations revealed a bond length of 1.355 Å in the ground state geometry and 1.325 Å in the excited state geometry, respectively. Additionally, as illustrated in Fig. 7-B, the geometry in the excited state

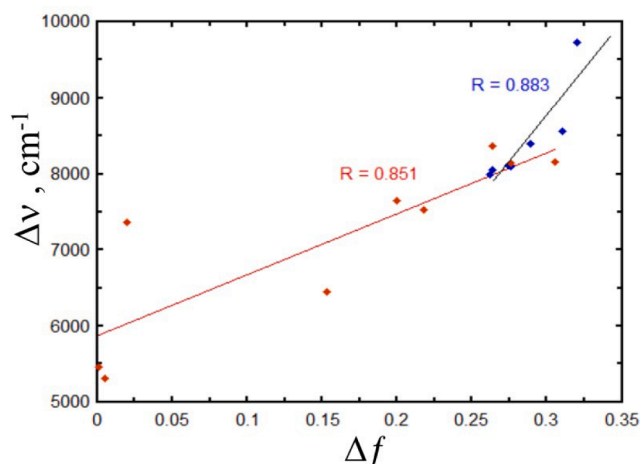


Fig. 6. Lippert-Mataga plot ( $\Delta\nu$  vs.  $\Delta f$ ) of II; red: non-polar and polar-aprotic, blue: polar-protic.

exhibited an increased bond order, indicative of potential charge transfer. As aforementioned, the positive solvatochromic behavior indicates that the dipole moment of the molecule in its ground state is less than in its excited state. Consequently, the increase in solvent polarity causes further stabilization of the excited state energy, which in turn

reduces the energy gap between the ground and excited states, resulting in a prolonged emission wavelength for the molecule of interest. In view of that, the results obtained from the DFT-geometry optimization of II in the ground and excited states revealed values of 7.29 and 5.98 Debye for  $\mu_e$  and  $\mu_g$ , respectively, which, in turn, is in good agreement in principle with the results obtained by the Catalán and Lippert-Mataga approaches concerning the positive fluorosolvatochromic behavior of II.

As experimentally observed, it is noteworthy to mention that such positive fluorosolvatochromic behavior for  $\lambda_{\text{Fluor}}$  may often be indicative of a  $\pi \rightarrow \pi^*$  electronic transition. Accordingly, TD-DFT calculations were conducted to gain insights concerning the key molecular orbitals (MOs) that are associated with the absorption and emission spectra and the corresponding electronic states and transitions of II. The IEFPCM solvation model was employed for accounting for the solvent effects on the spectral properties of II. Fig. 8 displays the experimental and simulated absorption and emission spectra of II. The vertical dotted lines correspond to the major electronic transition between MOs responsible for the absorption and emission bands. As can be noted, the simulated absorption spectra are in excellent agreement with the experimental analogues for  $\lambda_{\text{max}}$ ; however, a difference in the shape of the spectra can be noted regarding the shoulder that appears at  $\sim 280$  nm for the experimental spectrum compared to its simulated analogue. Importantly, although the shoulder does not appear clearly in the simulated spectrum, the DFT calculations revealed a transition at 280 nm with an oscillation frequency ( $f$ ) of 0.016. Such a low value of  $f$  might be the reason for not appearing as a shoulder in the spectrum, which in turn might be attributed to the limitations of the computational methods,

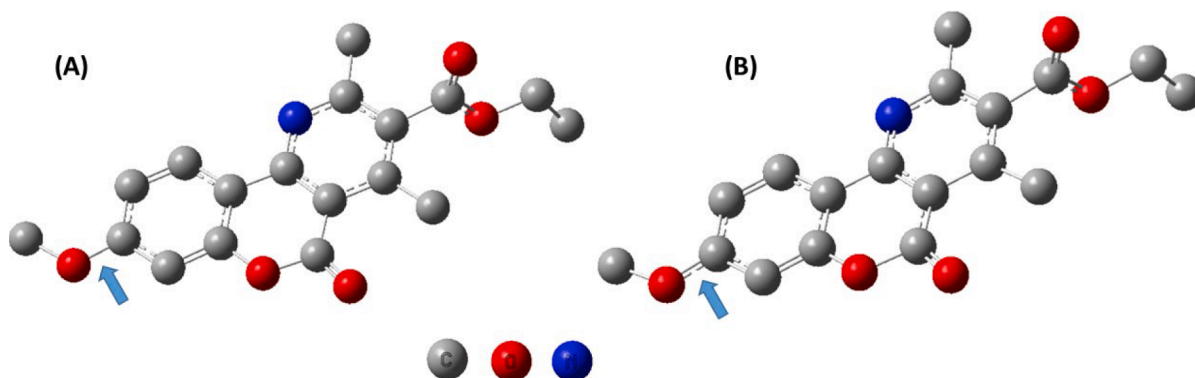


Fig. 7. Molecular geometry of II ((DFT (B3LYP/6-31G+(d), IEFPCM, methanol)) in the ground (A) and excited (B) states; hydrogen atoms are omitted for clarity.

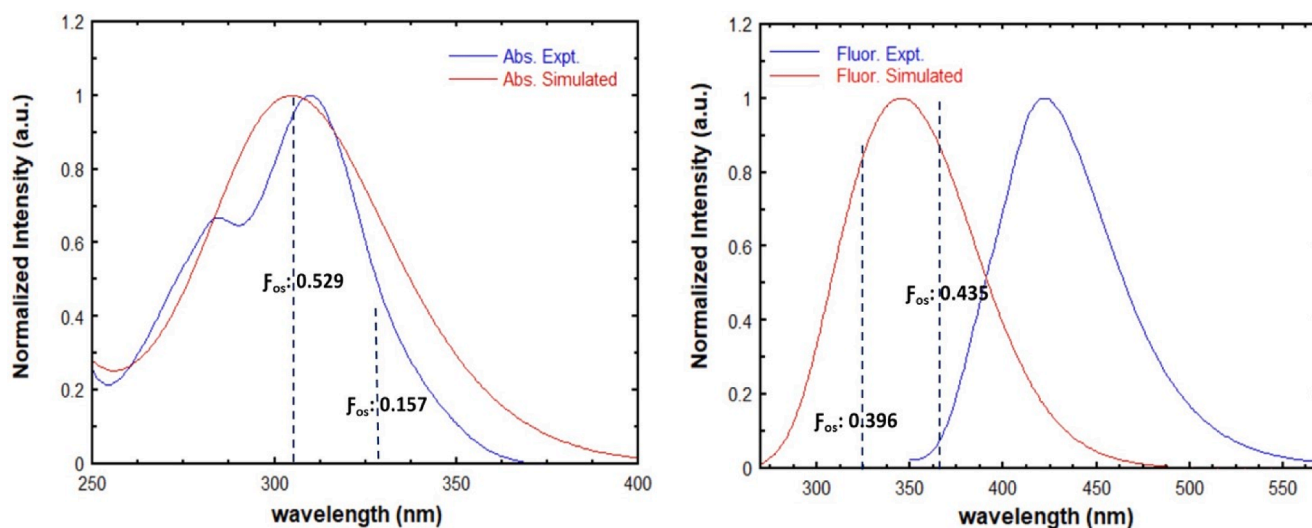


Fig. 8. Experimental and simulated TD-DFT (DFT (B3LYP/6-31G+(d), IEFPCM, methanol)) absorption and Fluorescence spectra of II.

including the solvation model PCM. It is noteworthy to mention that PCM assumes a static and continuum representation of the solvent, where the solvent is treated as a homogeneous medium with a fixed dielectric constant. As such, solvent effects are treated implicitly, and the explicit solvent molecules are not included in the calculations. Consequently, this may not fully capture the complex and dynamic behavior of solvent molecules, especially in cases where specific solvent-solute interactions exist, such as hydrogen bonding or ion-dipole interactions. Nevertheless, PCM remains a valuable tool in computational chemistry, particularly for studying solvation effects in molecular systems where explicit solvent molecules are computationally unnecessary. One can notice that although excellent agreement between the measured and simulated UV-Vis absorption spectra of II was observed, a significant difference between the experimental and theoretical maxima positions in the fluorescence spectra is notable. In fact, theoretical methods for calculating excited-state properties like fluorescence spectrum are inherently challenging. Hence, such methods might have limitations in describing excited-state phenomena accurately and might not fully capture the electronic interactions and environmental effects that influence the fluorescence properties of the molecule; this includes influential factors such as the solvent and conformational effects. The solvent environment can strongly influence the fluorescence behavior. If the theoretical calculations neglect or inadequately model the solvation effects, the predicted fluorescence maxima may deviate from the experimental values, which is an outcome that is not unusual upon employing implicit solvation models such as the PCM. On the other hand, molecules in solution can adopt different conformations due to solvent interactions, leading to variations in their fluorescence properties. Theoretical calculations might not consider the full conformational landscape or fail to accurately predict the dominant conformation present in the experimental conditions.

The TD-DFT calculations revealed that the key electronic transitions that contribute to the observed absorption band are the HOMO  $\rightarrow$  LUMO transition for  $\lambda_{329}$  with an oscillation frequency ( $f$ ) of 0.157, and HOMO  $\rightarrow$  LUMO and HOMO  $\rightarrow$  LUMO + 1 for  $\lambda_{302}$  with an  $f$  value of 0.529. For the emission spectra, reasonable agreement exists between the simulated and experimental  $\lambda_{\text{Fluor}}$ . Likewise, the key electronic contributions into the emission band are the LUMO  $\rightarrow$  HOMO and LUMO + 1  $\rightarrow$  HOMO transitions at  $\lambda_{363}$  and  $\lambda_{325}$  with  $f$  of 0.435 and 0.397, respectively. Additionally, in correspondence with the  $\pi \rightarrow \pi^*$  electronic transition concluded experimentally as the key electronic transition that contributes to the absorption and emission bands of II, further analysis is necessary concerning the nature of the molecular orbitals involved in such electronic transitions. The frontier orbitals, HOMO and LUMO, were generated as well as other molecular orbitals for II and III; see Fig. 9. As evident from Fig. 9, the HOMO and LUMO of II are  $\pi$  and  $\pi^*$  molecular orbitals, respectively, and they extend over the entire molecule, including the methoxy substituent. Intriguingly, this finding aligns well with the proposed ICT (intramolecular charge transfer) depicted in Scheme 1 and also correlates with the experimental and simulated spectral results obtained for II. However, for III, it can be noted that the HOMO is more localized around the methoxy group and partially extended over the phenyl moiety. This nature of the HOMO can potentially account for the poor fluorescence properties observed compared with II. Furthermore, we attempted to rationalize the effect of solvent polarity on the fluorosolvatochromic behavior of II by calculating the same MOs in 1,4-dioxane. Obtained results revealed similar shapes for the HOMO and LUMO; however, a stabilization of 0.098 eV and a destabilization of 0.048 eV in the LUMO and HOMO, respectively, were observed in methanol compared with 1,4-dioxane, which in turn is in good agreement with the experimental results, where a positive fluorosolvatochromic behavior is exhibited by II with increasing solvent polarity.

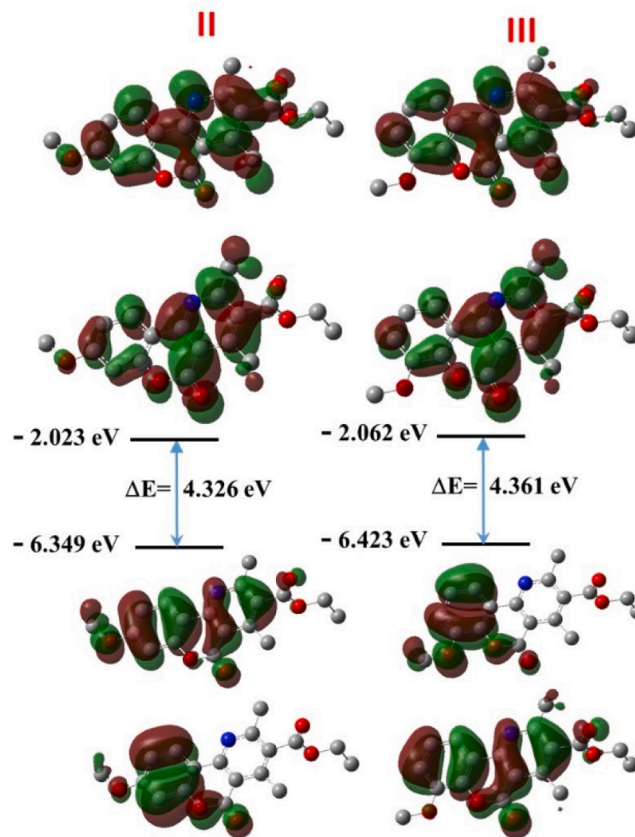


Fig. 9. Selected frontier MOs of II and III and the corresponding electronic transitions; DFT (B3LYP/6-31G+(d), IEFPCM, methanol).

#### 4. Conclusion

In this study, we investigated the medium effects on the physico-chemical and spectral properties of three derivatives of chromeno[4,3-b]pyridines. It was demonstrated that the position of the methoxy substituent on the chromeno moiety plays a crucial role in yielding derivatives with notable fluorescence properties. Specifically, the 7-methoxy-chromeno[4,3-b]pyridine-3-carboxylate derivative exhibited significantly higher fluorescence compared to the parent (unsubstituted) and 8-substituted analogues. Furthermore, the 7-substituted derivative displayed positive fluorosolvatochromic behavior, facilitated by intramolecular charge transfer (ICT) involving the methoxy substituent. This behavior was confirmed through steady-state fluorescence measurements and analyzed using linear solvation models. The emission spectra of the 7-substituted methoxy derivatives were influenced by the solvent's polarity, and the observed positive solvatochromic behavior indicated a more polar excited state with considerable structural changes. The experimental findings were further supported by DFT and TD-DFT computations, which rationalized the fluorosolvatochromic behavior in relation to electronic structures and electronic transitions. The results clearly demonstrated that the position of the methoxy substituent significantly contributes to the ICT of the chromeno[4,3-b]pyridine-3-carboxylate derivative and consequently to the correspondingly positive fluorosolvatochromic behavior.

#### CRediT authorship contribution statement

**Mohanad Shkoor:** Conceptualization, Investigation, Writing – review & editing. **Vandana Thotathil:** Investigation. **Raed M. Al-Zoubi:** Validation. **Haw-Lih Su:** Formal Analysis. **Abdulilah Dawoud Bani-Yaseen:** Conceptualization, Methodology, Data curation, Writing –



original draft, Supervision.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

No data was used for the research described in the article.

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## Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.saa.2023.123210>.

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