

Article

Synthesis, Photophysical Characterization, and Computational Analysis of Novel Bis(oxazolo[5,4-b]pyridine) Derivatives as Terpyridine-Inspired Fluorophores

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Abstract

Terpyridines are well-known ligands in coordination chemistry, are valued for their conformational flexibility and strong metal-binding properties, and are also of interest as fluorophores. This study focused on the synthesis and comprehensive investigation of a new class of bis-oxazolo[5,4-b]pyridine derivatives, designed based on their structural similarity to terpyridines. Four novel compounds, **4a–d**, were synthesized by cyclization of amide derivatives of 3-aminopyridin-2(1*H*)-ones using pyridine-2,6-dicarboxylic acid and its dichloride as key acidic components. Their structures and purity were confirmed by melting point analysis, high-resolution mass spectrometry, and ¹H, ¹³C NMR spectroscopy. Compounds **4a–c** exhibit UV absorption at 323–357 nm and intense blue to deep-blue fluorescence (357–474 nm, η $\approx$ 0.32–0.84) in chloroform, dichloromethane, and acetonitrile, attributed to p–p* transitions within the conjugated ring system. These findings suggest their potential as phosphors for organic electronics. Computational modeling of **4a–c** molecules provided insight into their electronic structures, conformational stability, and predicted optical behavior. The most stable conformers (**4a–II**, **4b–II**, **4c–II'**) exhibited a progressive decrease in the HOMO–LUMO gap from **4a** to **4c**, correlated with the enhancement of photoactivity. Among them, compound **4a** stands out as the most promising luminophore, displaying the most intense and narrow luminescence band, owing to its high molecular symmetry and stable emission characteristics. Overall, this study lays the foundation for future studies of bis(oxazolo[5,4-b]pyridine) derivatives in coordination chemistry and optoelectronic materials development.

Keywords: 3-aminopyridin-2(1*H*)-ones; oxazolo[5,4-b]pyridines; intramolecular heterocyclization; structural analogs of terpyridine; UV spectroscopy; optical properties; quantum exit; Stokes shift; in silico; computational study



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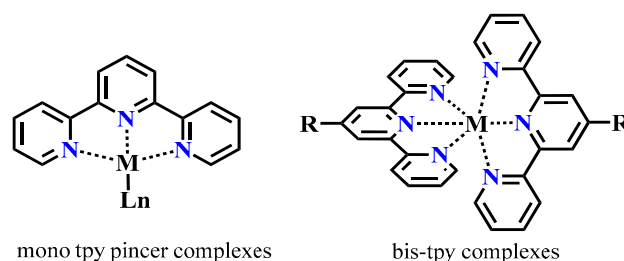
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1. Introduction

Creating advanced fluorophores and ligands that can be utilized in industrial processes, modern technologies, and daily life continues to be a key task in organic and

coordination chemistry. Many organic fluorophores are successfully used as biosensors, biomarkers, and dyes for labeling cells [1–5]. They are also widely used in organic electronics, including LEDs, transistors, batteries, solar cells, and other devices [6–8]. Their effectiveness is evaluated by such parameters as fluorescence quantum yield, Stokes shift, molar extinction coefficient, and absorption/emission maxima [1]. Since only a limited set of fluorophores reach optimal values, their practical applicability remains restricted. Thus, the development and evaluation of new fluorophores with improved photophysical properties remains a challenging and time-consuming process.

Organic fluorophores, often heterocyclic compounds, are widely used as ligands in coordination complexes with metal ions, where they play a crucial role in regulating metal ion reactivity [9]. Sometimes a single unique ligand can strongly determine the outcome of coordination processes by dictating the geometry, stability, and electronic properties of the resulting metal complexes [10–13]. Nitrogen-containing ligands are particularly important in coordination chemistry, varying from mono- to multidentate compounds depending on the number of coordination centers [14–16]. Among the nitrogen-based ligands, 2,2':6',2''-terpyridine **1** (tpy) has been extensively studied over the past 20 years [17–19] (Scheme 1).



Scheme 1. Basic coordination mode of terpyridine ligands.

Terpyridine derivatives and their metal complexes [20–22] have found wide application in fluorescent sensors and biological labels, photocatalysis, solar cell sensitization, molecular logic devices, organic light-emitting diodes (OLEDs), and various catalytic processes [23–25].

Overall, 2,2':6',2''-terpyridine derivatives and their metal complexes possess broad potential and practical applications, but difficulties including low synthetic yields and inadequate solubility persist. Accordingly, the development of novel terpyridine derivatives with dual roles—as organic fluorophores and effective coordinating ligands—constitutes an important direction in current organic and coordination chemistry. This is especially important in light of the growing demand for functional materials in organic electronics, molecular science, medicine, and drug discovery [26–28].

The aim of this study was to identify and comprehensively examine a series of structurally unique and previously undescribed bis-derivatives of oxazolo[5,4-b]pyridines. These compounds were selected as close structural analogues of terpyridines, which are well known for their versatility and effectiveness as ligands in coordination chemistry.

2. Materials and Methods

2.1. Material and Instrumentation

^1H and ^{13}C NMR spectra were recorded on Bruker AVANCE 500 (500 and 126 MHz, respectively, Ettlingen, Germany), Bruker Avance NEO (400 and 101 MHz, respectively, Ettlingen, Germany) and Magritek spinsolve 80 carbon ultra (81 and 20 MHz, respectively, Aachen, Germany) instruments using DMSO- d_6 . Residual solvent signals (2.49 and 39.5 ppm for ^1H and ^{13}C nuclei) served as an internal standard.

Sample were analyzed by HPLC-MS on an Agilent 1260 Infinity II (Agilent Technologies, Santa Clara, CA, USA) chromatograph coupled to an Agilent 6545 LC/Q-TOF (Agilent Technologies, Santa Clara, CA, USA) high-resolution mass spectrometer with a Dual AJS ESI (Agilent Technologies, Santa Clara, CA, USA) ionization source operating in positive ion mode using the following parameters: capillary voltage: 4000 V; spray pressure: 20 (psi); drying gas: 10 L/min; gas temperature: 325 °C; sheathed gas flow: 12 L/min; shielding gas temperature: 400 °C; nozzle voltage: 0 V, fragmentation voltage: 180 V; skimmer voltage: 45 V; octopole RF: 750 V. Mass spectra with LC/MS accuracy were recorded in the range 100–1000 m/z , scan rate 1.5 spectrum/s.

Chromatographic separation was carried out on columns: ZORBAX RRHD Eclipse Plus C18 (2.1 × 50 mm, particle size 1.8 µm, Agilent Technologies, Santa Clara, CA, USA). The column temperature during the analysis was maintained at 35 °C. The mobile phase was formed by eluents A and B. In the positive ionization mode, 0.1% formic acid solution in deionized water was used as eluent A, and 0.1% formic acid solution in acetonitrile was used as eluent B. Chromatographic separation was performed with elution according to the following scheme: 0–10 min 95% A, 10–13 min 100% B, 13–15 min 95% A. The flow of the mobile phase was maintained at 400 µL/min throughout the analysis. In all experiments, the sample injection volume was 1 µL. The sample was prepared by dissolving the entire sample (in 1000 µL) in methanol (for HPLC). Sample dilution was carried out immediately before analysis.

Melting points were determined on a Stuart SMP10 apparatus (Stuart Equipment, Staffordshire, UK). Elemental analysis was performed on a Carlo Erba 1106 CHN instrument (Carlo Erba Strumentazione, Milan, Italy). The reaction progress and product purity were monitored by TLC on Sorbfil plates and visualized using iodine vapor or UV light.

UV-Vis absorption spectra were recorded on a Shimadzu UV-2600 spectrophotometer (Shimadzu Corporation, Kyoto, Japan) in the range of 200–600 nm. Measurements were carried out in quartz cuvettes with a 1 cm optical path length, and the spectral slit width was 2 nm. The concentrations of the studied compounds were 2×10^{-5} M (for compounds **4a**, **4c**, and **4d**) and 1×10^{-5} M (for compound **4b**).

Fluorescence spectra were recorded on a Shimadzu RF-5301 PC spectrofluorimeter (Shimadzu Corporation, Kyoto, Japan). Measurements were performed at room temperature in quartz cuvettes with a 1 cm optical path length. The spectral range was 300–700 nm, and the spectral slit width was 3 nm. The concentrations of the studied compounds were 2×10^{-5} M (for compounds **4a**, **4c**, and **4d**) and 1×10^{-5} M (for compound **4b**).

The relative quantum yield was calculated using the following formula:

$$\varphi_i = \varphi_{st} \cdot \frac{A_{st}}{A_x} \cdot \frac{F_x}{F_{st}} \cdot \frac{n_x^2}{n_{st}^2}$$

where φ_i —is the fluorescence quantum yield of the studied compound (**4a–d**);

φ_{st} —is the fluorescence quantum yield of the standard used (quinine sulfate or tryptophan);

A_{st} , A_x —is the absorbances at excitation wavelength for the standard sample (st) and the studied compound (**4a–d**);

F_{st} , F_x —is the areas of fluorescence spectrum with spectral correction for the standard sample (st) and the studied compound (**4a–d**);

n_{st} , n_x —is the refractive index of the standard sample (st) and the studied compound (**4a–d**).

2.2. Synthesis and Spectral Analysis of Synthesized Compounds

3-Aminopyridine-2(1H)-ones **1a–d** were obtained by a similar procedure described in [29].

Synthesis of Diacyl Derivatives of Pyridine-2,6-Dicarboxylic Acid

General Procedure for Compounds 3a–d

A mixture of 1.0 mmol of 3-aminopyridin-2(1H)-one (**1a–d**) and 2.0 mmol of triethylamine (TEA) was dissolved in 10 mL of dichloromethane. 0.5 mmol of pyridine-2,6-dicarboxylic acid dichloride dissolved in 3 mL of dichloromethane was added dropwise while stirring and cooling. The reaction mixture was stirred at room temperature for 20–25 h. After completion, the mixture was washed with distilled water and extracted with dichloromethane. The combined organic layers were dried over Na₂SO₄, and the solvent was removed. The residue was recrystallized from a hexane–isopropanol mixture (1:2).

N²,N⁶-Bis(4,6-dimethyl-2-oxo-1,2-dihydropyridin-3-yl)pyridine-2,6-dicarboxamide 3a Yield: 232 mg (57%), colorless microcrystalline powder, mp 306–307 °C. ¹H NMR (500 MHz, DMSO-d₆) δ (J, Hz): 2.02 (s, 6H, 2CH₃), 2.16 (s, 6H, 2CH₃), 5.97 (s, 2H, H-5,5'), 8.21–8.29 (m, 3H, H-3,4,5 Py), 10.43 (s, 2H, 2NHCO), 11.73 (s, 2H, 2NHCO). ¹³C NMR (125 MHz, DMSO-d₆) δ: 18.2, 106.6, 122.1, 124.8, 139.6, 142.4, 147.6, 148.7, 160.4, 162.1. Found: C 61.72; H 5.02; N 17.70. Calculated for C₂₁H₂₁N₅O₄: C 61.91; H 5.20; N 17.19.

N²,N⁶-Bis(6-methyl-2-oxo-4-phenyl-1,2-dihydropyridin-3-yl)pyridine-2,6-dicarboxamide 3b Yield: 306 mg (62%), light gray microcrystalline powder, mp 238–239 °C. ¹H NMR (400 MHz, DMSO-d₆) δ: 2.25 (s, 6H), 6.10 (s, 2H), 7.28 (br. t, J = 3.1, 6H, Ph), 7.49–7.52 (m, 4H, Ph), 8.09 (br. s, 3H, H-3,4,5 Py), 10.34 (s, 2H), 11.96 (s, 2H). ¹³C NMR (100 MHz, DMSO-d₆) δ: 18.4, 105.6, 120.9, 124.4, 127.6, 128.1, 128.3, 137.3, 139.6, 143.7, 148.4, 149.9, 160.9, 162.7. Found: C 70.28; H 4.50; N 13.48. Calculated for C₃₁H₂₅N₅O₄: C 70.05; H 4.74; N 13.18.

N²,N⁶-Bis(6-methyl-2-oxo-4-(thiophen-2-yl)-1,2-dihydropyridin-3-yl)pyridine-2,6-dicarboxamide 3c Yield: 315 mg (58%), light gray microcrystalline powder, mp 255–256 °C. ¹H NMR (500 MHz, DMSO-d₆) δ: 2.24 (s, 6H), 6.54 (s, 2H), 7.10 (dd, J = 4.9, 4.0, 2H), 7.67 (d, J = 4.9, 2H), 7.74 (d, J = 3.1, 2H), 8.23–8.29 (m, 3H, H-3,4,5 Py), 10.62 (s, 2H), 11.78 (s, 2H). ¹³C NMR (125 MHz, DMSO-d₆) δ: 18.5, 102.3, 119.2, 124.6, 127.0, 128.9, 130.4, 139.6, 141.3, 143.2, 148.7, 160.8, 163.2. Found: C 59.80; H 3.67; N 13.03. Calculated for C₂₇H₂₁N₅O₄S₂: C 59.66; H 3.89; N 12.88.

N²,N⁶-Bis(6-methyl-4-(5-methylfuran-2-yl)-2-oxo-1,2-dihydropyridin-3-yl)pyridine-2,6-dicarboxamide 3d Yield: 318 mg (59%), light gray microcrystalline powder, mp 258–260 °C. ¹H NMR (80 MHz, DMSO-d₆) δ: 2.25 (br. s, 12H), 6.54 (d, J = 3.1, 2H), 6.42 (s, 2H), 6.92 (d, J = 3.1, 2H), 8.28 (br. s, 3H, H-3,4,5 Py), 10.56 (br. s, 2H), 11.75 (br. s, 2H). ¹³C NMR (20 MHz, DMSO-d₆) δ: 13.3, 18.6, 100.1, 109.0, 114.8, 117.5, 124.8, 137.2, 139.8, 143.7, 146.8, 148.9, 153.7, 160.8, 162.5. Found: C 64.89; H 4.94; N 13.23. Calculated for C₂₉H₂₅N₅O₆: C 64.56; H 4.67; N 12.98.

Synthesis of 2,5-Bis(oxazolo[5,4-b]pyridine) Derivatives

General Procedure for Compounds 4a–d

A mixture of 1.0 mmol of N²,N⁵-bis(2-oxo-1,2-dihydropyridin-3-yl)pyridine-2,5-dicarboxamide (**3a–d**) and 5.0 mmol of phosphorus oxychloride was heated at 90–100 °C under reflux with a calcium chloride drying tube for 5 h. Excess phosphorus oxychloride was removed under vacuum. The reaction mixture was treated with cold water, and the resulting precipitate was filtered, washed with distilled water, and air-dried. The product was recrystallized from a mixture of isopropanol and dichloromethane (2:3).

2-(6-(5,7-Dimethyl-3a,4-dihydrooxazolo[5,4-b]pyridin-2-yl)pyridin-2-yl)-5,7-dimethylloxazolo[5,4-b]pyridine 4a Yield: 304 mg (82%), colorless crystals, mp 259–260 °C. ¹H NMR (500 MHz, DMSO-d₆) δ (J, Hz): 2.03 (s, 6H, 2 CH₃), 2.16 (s, 6H, 2 CH₃), 7.30 (s, 2H), 8.32 (t, J = 2.7, 1H, H-4 of Py), 8.53 (d, J = 7.8, 2H, H-3,5 of Py). High-resolution mass spectrum (ESI-QTOF): found *m/z* [M + H]⁺ 372.1453; calculated for C₂₁H₁₈N₅O₂⁺: 372.1455.

5-Methyl-2-(6-(5-methyl-7-phenyl-3a,4-dihydrooxazolo[5,4-b]pyridin-2-yl)pyridin-2-yl)-7-phenyloxazolo[5,4-b]pyridine 4b Yield: 342 mg (69%), white microcrystalline powder, mp 288–289 °C. ¹H NMR (400 MHz, DMSO-d₆) δ (J, Hz): 2.70 (s, 6H, 2CH₃), 7.57 (t, J = 7.1,

2H, H-4,4' of Ph), 7.64 (t, $J = 7.3$, 4H, H-3,5,3',5' of Ph), 7.80 (s, 2H, H-6,6'), 8.30 (d, $J = 7.8$, 4H, H-2,6,2',6' of Ph), 8.34–8.36 (m, 1H, H-4 of Py), 8.60 (d, $J = 7.8$, 2H, H-3,5 of Py). Found: C 75.42; H 3.98; N 14.46. Calculated for $C_{31}H_{21}N_5O_2$: C 75.14; H 4.27; N 14.13.

2,6-Bis(5-methyl-7-(thiophen-2-yl)-3a,4-dihydrooxazolo[5,4-b]pyridin-2-yl)pyridine 4c Yield: 368 mg (72%), light gray microcrystalline powder, mp 363–365 °C. 1H NMR (80 MHz, DMSO- d_6) δ (J, Hz): 2.65 (br. s, 6H, 2CH₃), 7.35 (br. s, 2H, H-4',4'' of thiophene), 7.74 (s, 2H, H-6,6'), 7.93 (d, $J = 4.0$, 2H, H-3',3'' of thiophene), 8.25 (d, $J = 4.5$, 2H, H-5',5'' of thiophene), 8.30–8.61 (m, 3H, H-3,4,5 Py). Found: C 63.75; H 4.38; N 13.47. Calculated for $C_{27}H_{21}N_5O_2S_2$: C 63.39; H 4.14; N 13.69.

2,6-Bis(5-methyl-7-(5-methylfuran-2-yl)-3a,4-dihydrooxazolo[5,4-b]pyridin-2-yl)pyridine 4d Yield: 431 mg (85%), white microcrystalline powder, mp 296–298 °C. 1H NMR (80 MHz, DMSO- d_6) δ (J, Hz): 2.41 (s, 6H, 2 CH₃); 2.62 (s, 6H, 2 CH₃); 6.26 (d, 2H, $J = 2.5$ Hz, H-4',4'' Fu); 7.47 (s, 2H, H-6,6'); 7.63 (d, 2H, $J = 2.9$, H-3',3'' Fu); 8.16 (t, 1H, $J = 7.7$, H-4 Py); 8.53 (d, $J = 7.4$, 2H, H-3,5 Py). Found: C 68.92; H 5.18; N 14.06. Calculated for $C_{29}H_{25}N_5O_4$: C 68.63; H 4.97; N 13.80.

2.3. Conformational Analysis and Electronic Structure of the New 2,6-Bis(oxazolo[5,4-b]pyridin-2-yl)pyridines

Geometry optimizations and frequency calculations (OPT + FREQ) were performed using DFT with the ω B97XD functional [30] and 6-311++G(d,p) basis set [31] in Gaussian 16 [32]. Molecular structures were built and visualized in GaussView 6.0 [33].

The ω B97XD functional was chosen for its reliable treatment of dispersion forces, conformational flexibility, and π -delocalization, which are key features in modeling heteroaromatic systems such as 2,6-bis(oxazolo[5,4-b]pyridin-2-yl)pyridines. Its long-range correction and empirical dispersion terms ensure accurate representation of noncovalent and stacking interactions [34].

Optimizations were first performed in vacuum to assess intrinsic conformational preferences. Solvent effects were then evaluated via geometry optimizations CPCM calculations [35] in dichloromethane and acetonitrile, representing spectroscopic medium.

All optimized geometries were confirmed as true minima by the absence of imaginary frequencies [36]. Thermochemical data, dipole moments, and electronic descriptors were extracted from the output files [37].

HOMO and LUMO frontier molecular orbitals were visualized to assess electron distribution, energy gaps, and donor–acceptor potential. Orbital localization was analyzed to identify reactive centers and evaluate π -conjugation. Molecular electrostatic potential (MEP) maps were generated on the electron density isosurface (0.001 Hartree) to visualize charge distribution [38]. Color-coded gradients highlight nucleophilic and electrophilic regions, aiding interpretation of coordination and supramolecular behavior [39].

2.4. DFT-Based Simulation of Electronic Absorption and Luminescence Properties

UV–vis absorption and emission spectra were simulated using time-dependent density functional theory (TD-DFT) as implemented in Gaussian 16 [40]. All calculations were performed with the long-range corrected ω B97XD functional and the 6-311++G(d,p) basis set, incorporating solvent effects via the conductor-like polarizable continuum model (CPCM) with acetonitrile as the solvent.

Initial geometry optimizations of the ground state (S_0) were carried out using DFT at the ω B97XD/6-311++G(d,p) level with CPCM (acetonitrile) solvation. Vertical excitation energies and oscillator strengths were then computed via TD-DFT using the keyword TD = (NStates = 30, Root = 1) to simulate the UV–vis absorption spectrum. The resulting transitions from S_0 to excited singlet states (S_n) were analyzed to identify key absorption bands.

To simulate luminescence, the geometry of the first excited state (S_1) was optimized using DFT at the ω B97XD/6-311++G(d,p) level with CPCM (acetonitrile) solvation. Following excited-state optimization, vertical transitions from the relaxed excited state back to the ground state ($S_1 \rightarrow S_0$) were computed using TD-DFT. These transitions represent the emission processes and were used to construct theoretical luminescence spectra.

Excitation energies and oscillator strengths were extracted from Gaussian output files. Spectral profiles were visualized using MS Excel software.

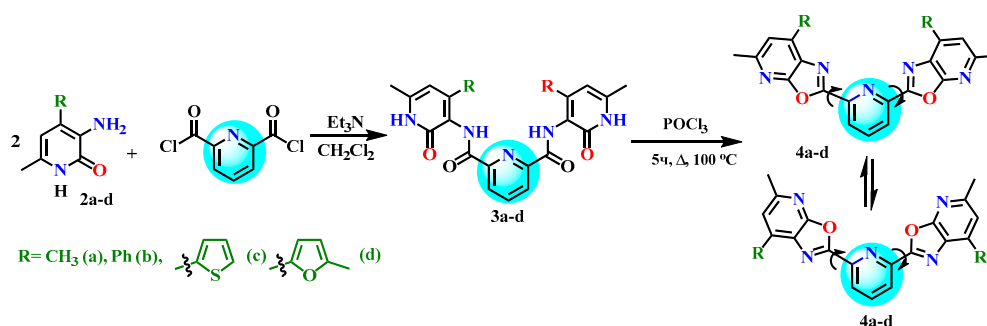
3. Results and Discussion

3.1. Chemistry

Our previous studies demonstrated that 4-aryl(hetaryl)-substituted 3-aminopyridin-2(1H)-ones remain largely unexplored in the literature [26], but they represent promising synthons for the development of efficient luminophores [29]. The simplest derivative, 4-phenyl-3-aminopyridin-2(1H)-one, showed a notably high fluorescence quantum yield of 76% [41]. The amino acid-like fragment present in the 3-aminopyridone framework makes these compounds important precursors for designing peptidomimetics [42–44] and more complex biologically active heterocyclic systems [45–47].

The aim of this study was to synthesize structural analogues of terpyridines using our previously developed cyclization methods for amide derivatives of 3-aminopyridin-2(1H)-ones [48–51]. For this purpose, pyridine-2,6-dicarboxylic acid and its dichloride derivative were selected as the acid components.

We have previously established that 4-aryl-substituted 3-aminopyridin-2(1H)-ones **2a–d** undergo acylation with pyridine-2,6-dicarboxylic acid dichloride in the presence of triethylamine, forming the corresponding diamides **3a–d**. Further heating of these diamides with phosphorus oxychloride leads to cyclization products of 2,6-bis(oxazolo[5,4-b]pyridin-2-yl)pyridines **4a–d** with the yields of around 80% (Scheme 2).



Scheme 2. Synthesis of 2,6-bis(oxazolo[5,4-b]pyridin-2-yl)pyridine derivatives **4a–d**.

A comparative analysis of the synthesized 2,6-bis(oxazolo[5,4-b]pyridin-2-yl)pyridines **4a–d** showed that they are structurally very similar to terpyridines. However, unlike terpyridine, these compounds contain three heteroatoms (one oxygen and two nitrogen atoms) in each peripheral condensed oxazolopyridine ring system. This structural feature may lead to improved coordination and luminescent properties due to the increased number of conjugated bonds, the presence of additional electron-accepting oxygen and nitrogen atoms, and the potential for new conformations resulting from rotation around the C(2) and C(6) bonds of the central pyridine core.

3.2. Photophysical Properties of Compounds

The synthesized 2,6-bis(oxazolo[5,4-b]pyridin-2-yl)pyridines (**4a–d**) show strong fluorescence in the blue and deep-blue region when exposed to UV light (Figure 1). This

property is particularly important for potential applications in organic electronics, given the well-recognized shortage of organic luminophores that emit in the blue range. In addition, these compounds may serve as promising chelating agents and fluorescent markers for various metal cations, including rare-earth elements, with the potential to enhance luminescence upon complex formation.



Figure 1. Observed luminescence of 2,6-bis(oxazolo[5,4-b]pyridin-2-yl)pyridine samples under UV irradiation.

The spectral properties, including λ_{max} , Stokes shift, and quantum yield of the synthesized compounds **4a–d** in chloroform, dichloromethane and acetonitrile were measured, as they are of interest as potential luminophores. The initial step involved recording the UV–Vis absorption spectra of the bis(oxazolopyridine) derivatives **4a–d** in chloroform, dichloromethane, and acetonitrile. The measurements were carried out at a concentration of 2×10^{-5} M for compounds **4a**, **4c**, and **4d**, and 1×10^{-5} M for compound **4b**. The spectral characteristics of the compounds **4a–d** are summarized in Table 1. The absorption spectra of compounds **4a–d** are shown in Figure 2.

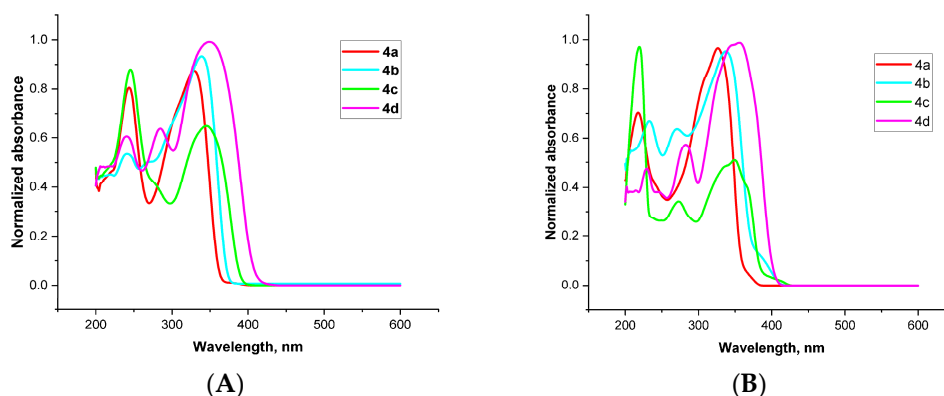


Figure 2. Cont.

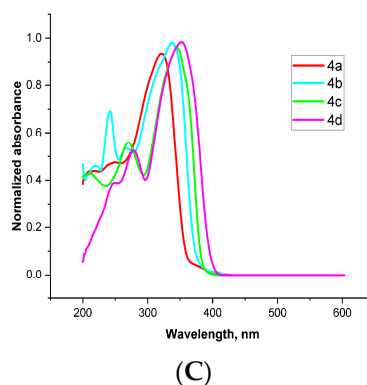


Figure 2. Normalized absorption spectra of bisoxazolo [5,4-b]pyridine derivatives **4a–d** in chloroform (A), dichloromethane (B), acetonitrile (C).

Table 1. Photophysical properties of compounds **4a–d**.

Compound	UV–Vis					
	λ^{abs}_{max} [nm]			ϵ , [L/cm ² mol]		
	CHCl ₃	CH ₂ Cl ₂	CH ₃ CN	CHCl ₃	CH ₂ Cl ₂	CH ₃ CN
4a	329	327	323	4200	3750	4950
4b	338	337	336	5100	5000	7500
4c	351	350	347	5000	4500	11150
4d	343	357	354	4700	4100	4450

Compound	Photoluminescence								
	λ^{em}_{max} [nm]			Stokes shift, [cm ^{−1}]			Quantum yield (Φ_f) ^a		
	CHCl ₃	CH ₂ Cl ₂	CH ₃ CN	CHCl ₃	CH ₂ Cl ₂	CH ₃ CN	CHCl ₃	CH ₂ Cl ₂	CH ₃ CN
4a	358; 372	357; 372	368	3513	3699	3786	0.50	0.84	0.71
4b	368; 386	367; 384	365; 382	3679	3632	3584	0.63	0.63	0.44
4c	391; 414	415	431	4335	4475	5617	0.40	0.38	0.32
4d	444	454	474	6632	5985	7152	0.47	0.73	0.74

^a The fluorescence quantum yield was calculated relative to the standard (quinine sulfate in 0.1M H₂SO₄, Φ_f = 0.55, tryptophan pH = 6.1, Φ_f = 0.15) [25–27].

It was found that all synthesized 2,2′-bis(oxazolo [5,4-b]pyridine) derivatives show absorption maxima in the range of 323–357 nm. This is attributed to π – π^* electronic transitions within the conjugated bis(oxazolo [5,4-b]pyridine) ring system. According to spectral analysis, compounds **4c** and **4d** display pronounced absorption in the longer wavelength region. Compound **4c** showed λ^{abs}_{max} = 351 nm in chloroform, 350 nm in dichloromethane, and 347 nm in acetonitrile, while compound **4d** exhibited λ^{abs}_{max} = 343 nm in chloroform, 357 nm in dichloromethane, and 354 nm in acetonitrile. These values are shifted relative to compound **4a**, which exhibits λ^{abs}_{max} = 329 nm in chloroform, 327 nm in dichloromethane, and 323 nm in acetonitrile. The methyl group at the 4-position of the pyridine ring in **4a** does not participate in conjugation with the π -system, which explains the shorter wavelength absorption. The bathochromic shift observed in compounds **4c** and **4d** is may be due to the presence of heteroatoms (sulfur and oxygen) with lone electron pairs that engage in additional n– π conjugation with the pyridine ring. The difference in absorption maxima between the thiophene and furan rings is related to the higher polarizability of the sulfur atom compared to oxygen. Compound **4b** also shows a bathochromic shift relative to **4a**, which is caused by π – π conjugation between the phenyl group and the pyridine ring.

Since the synthesized compounds **4a–d** contain two conjugated oxazolo [5,4-b]pyridine ring systems and are of considerable interest as potential luminophores, we aimed to

determine their fluorescence quantum yields. This parameter, defined as the ratio of emitted photons to absorbed photons, indicates how efficiently a substance converts absorbed light energy into fluorescent emission.

Quantum yield measurements for compounds **4a–d** were carried out by recording fluorescence spectra in chloroform, dichloromethane, and acetonitrile, with solution concentrations of 2×10^{-5} M for **4a**, **4c**, and **4d**, and 1×10^{-5} M for **4b**. The excitation wavelengths were selected to match the absorption maxima of each compound (Figure 3). The emission maxima of the studied compounds fall within the range of 323 to 357 nm, corresponding to blue and deep-blue photoluminescence (Table 1).

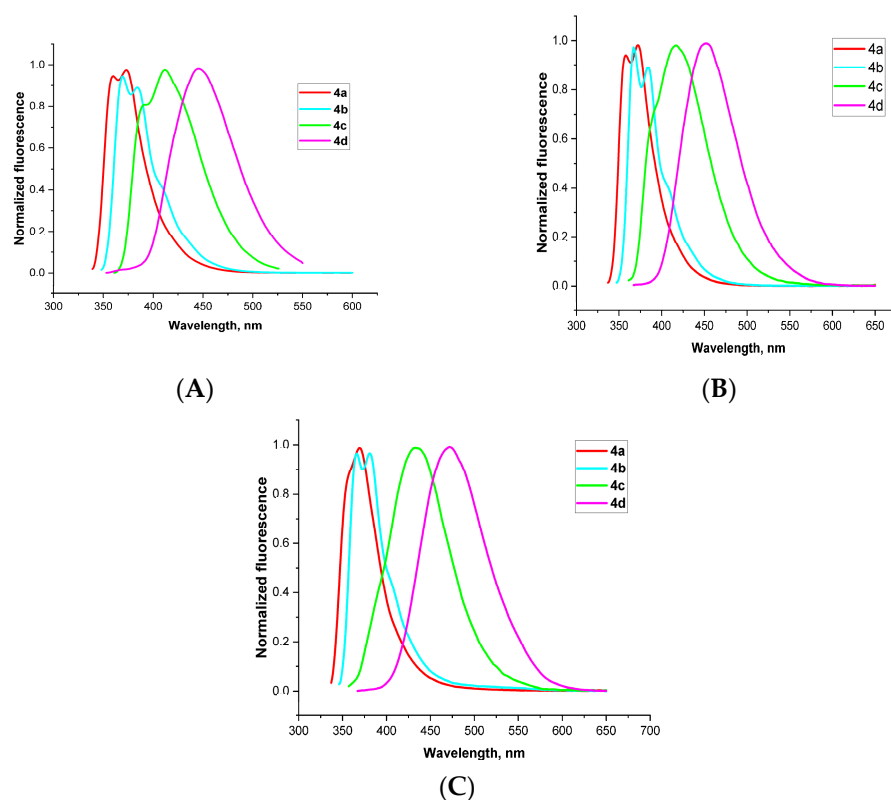


Figure 3. Normalized fluorescence spectra of bisoxazolo [5,4-b]pyridine derivatives **4a–d** in chloroform (A), dichloromethane (B), acetonitrile (C).

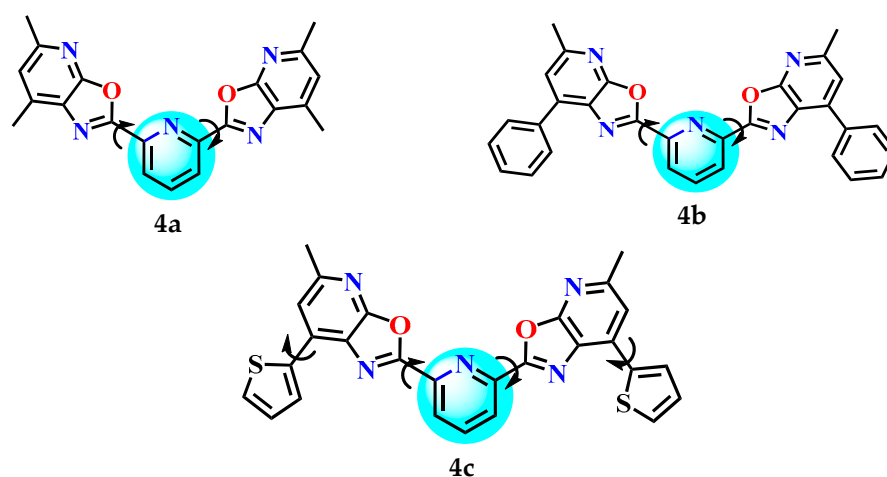
Thus, we confirmed the photoluminescent properties of the newly synthesized 2,2'-bis(oxazolo [5,4-b]pyridine) derivatives **4a–d** and found that they exhibit high fluorescence quantum yields ($\varphi_i \approx 0.32$ – 0.84), surpassing well-known standards such as quinine sulfate ($\varphi_i \approx 0.55$) and tryptophan ($\varphi_i \approx 0.15$). These findings indicate that new compounds based on 2,6-bis(oxazolo [5,4-b]pyridin-2-yl)pyridines **4a–d** are promising both as efficient luminophores and as potential ligands for metal complexation.

3.3. Conformational Analysis and Electronic Structure of the New 2,6-Bis(oxazolo[5,4-b]pyridin-2-yl)pyridines

The photophysical study of compounds **4a–d** demonstrated that changes in the 2,2'-bis(oxazolo [5,4-b]pyridine) structure influence their spectral characteristics, fluorescence efficiency, and solvent sensitivity. Compounds **4a–c** exhibited shorter-wavelength fluorescence ($\lambda_{max}^{em} \approx 358$ – 414 nm) in the blue and deep-blue region, while compound **4d** displayed a more red-shifted emission ($\lambda_{max}^{em} \approx 444$ – 474 nm), extending into the blue-green region. Since our focus was on blue and deep-blue luminophores, we selected compounds **4a–c** for further computational modeling in order to gain deeper insight into

their electronic structure, assess the stability of possible conformations, and simulate their absorption and fluorescence spectra. The calculations were carried out using density functional theory (DFT) with the ω B97XD functional [30] and the 6-311++G(d,p) basis set [31] in Gaussian 16 [32]. Molecular structures were built and visualized using GaussView 6.0 [33].

Scheme 3 illustrates the general conformational landscape of compounds **4a**, **4b**, and **4c**, which was further used for conformer search and computational modeling.



Scheme 3. Conformational landscape of compounds **4a**, **4b** and **4c**.

As shown in Scheme 3, compounds **4a**, **4b**, and **4c** share a terpyridine-like scaffold, where the central pyridine ring is symmetrically substituted at positions 2 and 6 with fused oxazolo[5,4-*b*]pyridine units carrying different substituents at positions 5 and 7 of the oxazole ring. Compound **4a** (2,6-bis(5,7-dimethyloxazolo[5,4-*b*]pyridin-2-yl)pyridine) carries methyl substituents at both the 5- and 7-positions of each oxazolopyridine unit, which enhance the overall molecular symmetry and increase the electron-donating character. Compound **4b** (2,6-bis(5-methyl-7-phenyloxazolo[5,4-*b*]pyridin-2-yl)pyridine) contains a phenyl substituent at position 7, introducing extended π -conjugation and potential for intermolecular interactions via aromatic stacking. Compound **4c** (2,6-bis(5-methyl-7-(thiophen-2-yl)oxazolo[5,4-*b*]pyridin-2-yl)pyridine) incorporates a thiophene ring at position 7, which may influence electronic properties through sulfur-based heteroaromatic conjugation and increase polarizability. These structural variations are designed to modulate the electronic properties of the terpyridine analogues, with potential applications in luminescent materials and metal complexation.

Based on these structural features, detailed rotational transformation Schemes S1–S3 were developed to systematically explore the conformational landscape of compounds **4a–c**. These schemes account for the torsional flexibility of the substituents at the 2 and 6 positions of the central pyridine ring, as well as the additional rotational freedom introduced by the thiophene groups in compound **4c**. Transitions between forms occur due to rotation around the C(2)–C and C(6)–C bonds of the central pyridine ring.

The thermodynamic stability of the conformations of compounds **4a–c** in different media was evaluated based on their total electronic energy (*E*) and Gibbs free energy (*G*), calculated using DFT level of theory with the ω B97XD functional and the 6-311++G(d,p) basis set in Gaussian 16 (Table S2). Table 2 presents the relative total energies (ΔE) and Gibbs free energies (ΔG) of the conformers of compounds **4a–c** in vacuum and in solvents (CH_2Cl_2 , CH_3CN). In all cases, the most stable conformers have ΔE (ΔG) = 0 and serve as the reference point.

Table 2. The differences in total energies (ΔE) and Gibbs free energies (ΔG) of the conformers of compounds **4a–c** in vacuum and in solvents (CH_2Cl_2 , CH_3CN), calculated relative to the lowest-energy conformer.

No	Conformation	ΔE , kJ/mol			ΔG , kJ/mol		
		Vacuum	CH_2Cl_2	CH_3CN	Vacuum	CH_2Cl_2	CH_3CN
Compound 4a							
1.	4a-I	10.4784	5.7446	5.2773	3.3291	2.4968	2.1477
2.	4a-II	0	0	0	0	0	0
3.	4a-III	4.7653	2.6518	2.4601	1.5464	2.1529	2.0873
Compound 4b							
4.	4b-I	10.9037	4.2297	3.4552	17.8797	2.0794	2.2054
5.	4b-II	0	0	0	0	0	0
6.	4b-III	4.3715	2.7725	2.4969	2.3341	0.9636	1.6829
Compound 4c							
7.	4c-I	13.8023	5.3691	4.0196	14.3379	5.3035	13.1249
8.	4c-I'	9.4912	7.3304	3.0430	16.2203	7.1414	4.2139
9.	4c-II	3.3423	1.2944	2.2238	4.8703	2.2789	6.7685
10.	4c-II'	0	0	0	0	0	0
11.	4c-III	8.5040	4.0748	3.4237	8.2283	3.0718	3.7256
12.	4c-III'	1.9429	2.4680	2.5310	2.1345	0.2232	1.0896
13.	4c-III''	5.1355	2.7358	2.33938	2.6833	1.4073	1.4283

The data presented in Table 2 show that each compound has a preferred conformation with the lowest Gibbs free energy in a given solvent. Specifically, the most stable conformer is **4a–II** for compound **4a**, **4b–II** for compound **4b**, and **4c–II'** for compound **4c**.

The presence of solvents reduces the energy differences between conformers, making the less stable forms more accessible. For compounds **4a** and **4b**, the energy gaps between conformers are relatively small (2–6 kJ/mol in solvents), which suggests that several conformers may coexist. In contrast, compound **4c** shows a broader range of conformers with similar energies, particularly in solvents, which may be due to the increased flexibility of the molecular framework and the presence of multiple local minima on the potential energy surface. This may account for the complexity of its spectral interpretation and indicate possible conformational dynamics.

Figure 4 shows the optimized geometries of the most stable conformers **4a–II**, **4b–II**, and **4c–II'**, obtained by DFT geometry optimization ($\omega\text{B97XD}/6\text{-}311++\text{G(d,p)}$) in acetonitrile. Tables S2–S4 provide the atomic Cartesian coordinates of the optimized geometries of compounds **4a–II**, **4b–II**, and **4c–II'**, together with their corresponding total energies in Hartree.

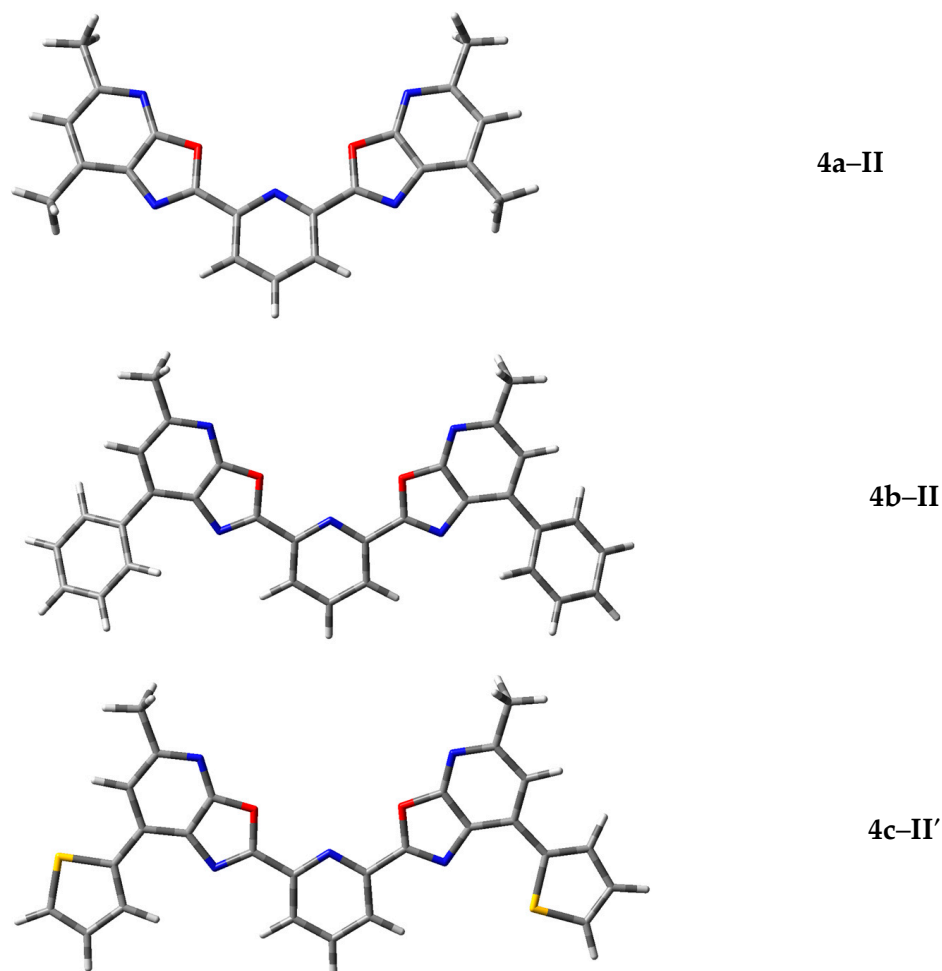


Figure 4. Optimized geometries of the most stable conformations of compounds **4a–c** calculated by DFT (ω B97XD/6-311++G(d,p)) in acetonitrile (CH_3CN).

The structures shown in Figure 4 highlight key features of spatial organization that affect the photophysical properties and thermodynamic stability of the compounds. Conformation **4a-II** is compact and symmetric, with a planar arrangement of oxazole fragments. This promotes effective conjugation and minimizes steric interactions between substituents, which explains its lowest Gibbs free energy among the **4a** conformers. Conformation **4b-II** has an extended molecular geometry with a well-developed π -conjugated system. The substituents are positioned to avoid steric clashes while maintaining electronic delocalization. This geometry supports high molar extinction and moderate fluorescence quantum yield. Conformation **4c-II'** is the most branched and spatially crowded structure. The presence of additional donor–acceptor fragments causes molecular bending and leads to an increased Stokes shift. All three conformers show a favorable balance between electronic conjugation and spatial stability, as confirmed by their minimal Gibbs energy values.

To better understand how spatial arrangement affects the electronic properties of these compounds, the next step was to compare the optimized geometries of conformers **4a-II**, **4b-II**, and **4c-II'** with the distribution of their HOMO–LUMO frontier molecular orbitals. These orbitals were calculated based on the optimized geometries using DFT (ω B97XD/6-311++G(d,p)) in Gaussian 16, and visualized in GaussView 6.0 (Figure 5).

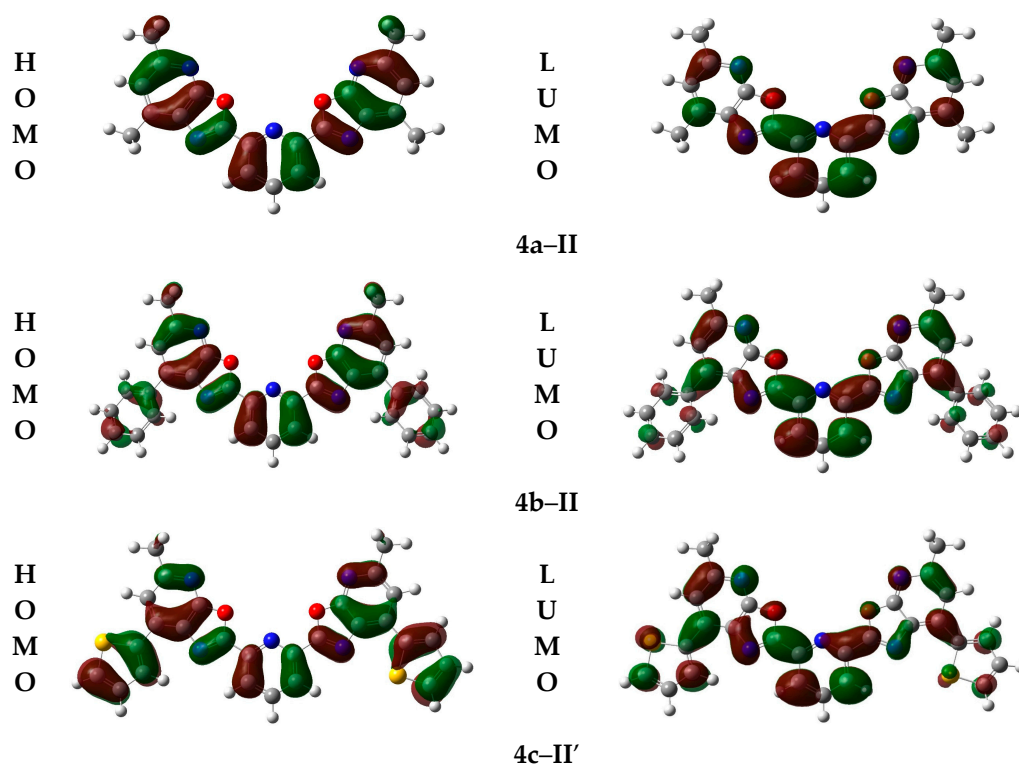


Figure 5. HOMO–LUMO frontier molecular orbitals visualization for the most stable conformations **4a-II**, **4b-II** and **4c-II'**, calculated by DFT (ω B97XD/6-311++G(d,p)) in acetonitrile (CH_3CN).

The diagrams shown in Figure 5 illustrate the spatial distribution of the frontier molecular orbitals, revealing characteristic electronic features of compounds **4a-c**. In all structures, the HOMO is mainly localized on the aromatic and heterocyclic fragments, indicating their donor nature and involvement in electronic transitions. The LUMO is distributed over the p-conjugated system, including acceptor regions, which confirms the dominance of $p \rightarrow \pi^*$ transitions. Conformation **4c-II'** is particularly notable for its more pronounced spatial separation between HOMO and LUMO, which may contribute to an increased Stokes shift and enhanced fluorescence efficiency.

Table 3 presents the calculated HOMO and LUMO energy values for the most stable conformations **4a-II**, **4b-II** and **4c-II'**, along with their corresponding energy gaps.

Table 3. Energy characteristics of HOMO and LUMO orbitals for the most stable conformations **4a-II**, **4b-II** and **4c-II'**.

Conformation	E (HOMO), eV	E (LUMO), eV	ΔE (LUMO–HOMO), eV
4a-II	−8.32	−0.62	7.70
4b-II	−8.38	−0.75	7.63
4c-II'	−8.20	−0.88	7.32

As shown in Table 3, the energy gap between the HOMO and LUMO orbitals decreases consistently from conformation **4a-II** to **4c-II'**, reflecting differences in the electronic structure and photophysical behavior of the compounds. The largest gap is observed for conformation **4a-II** ($\Delta E = 7.70$ eV), indicating high ground-state stability and a tendency toward shorter-wavelength absorption. Conformation **4b-II** shows an intermediate gap ($\Delta E = 7.63$ eV), which may suggest easier excitation and a shift toward longer wavelengths. The smallest gap is found in conformation **4c-II'** ($\Delta E = 7.32$ eV), indicating a

higher tendency for electronic excitation, which may enhance fluorescence and increase the Stokes shift.

Overall, the decreasing HOMO–LUMO gap from **4a-II** to **4c-II'** indicates enhanced photoactivity. The narrowest gap observed for **4c-II'** is consistent with the previously noted spatial separation of the HOMO and LUMO orbitals, which may support more efficient charge transfer in the excited state and stronger fluorescence.

To further explore the distribution of electron density and identify potential reactive sites in the molecules, a molecular electrostatic potential (MEP) analysis was performed for the most stable conformations **4a-II**, **4b-II** and **4c-II'** (Figure 6). It was shown, that the molecular electrostatic potential (MEP) surfaces of the studied conformers exhibit comparable ranges. The potential ranges from -0.095 to $+0.095$ Hartree (-248.0 to $+248.0$ kJ/mol) for conformer **4a-II**, from -0.092 to $+0.092$ Hartree (-240.7 to $+240.7$ kJ/mol) for conformer **4b-II** and from -0.091 and $+0.091$ Hartree (-238.9 to $+238.9$ kJ/mol) for conformer **4c-II'**. These values indicate that all three compounds possess similar charge distributions and polarity across their molecular surfaces.

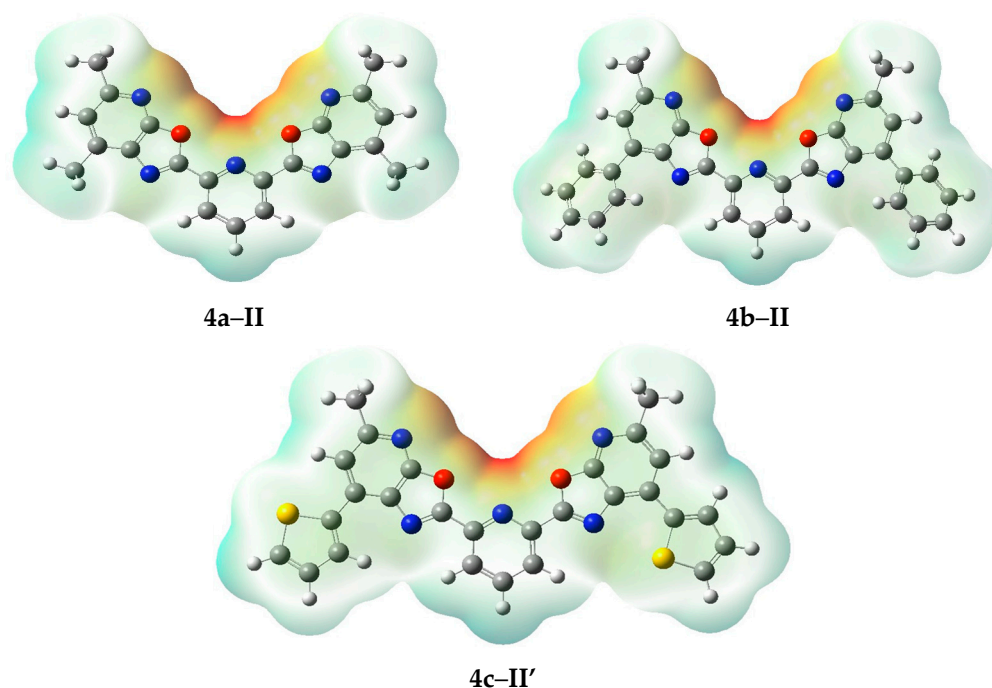


Figure 6. Molecular Electrostatic Potential (MEP) maps for the most stable conformations **4a-II**, **4b-II** and **4c-II'** calculated by DFT (ω B97XD/6-311++G(d,p)) in acetonitrile (CH_3CN) MEP color scale: red areas indicate regions with the most negative potential; blue areas show regions with positive potential; green and yellow zones represent neutral charge distribution.

As can be seen in Figure 6, the regions of most negative potential (red zones) of conformations **4a-II**, **4b-II** and **4c-II'** are localized near electronegative atoms such as oxygen and nitrogen, indicating possible sites for nucleophilic attack and hydrogen bond acceptance. Conversely, the most positive potential areas (blue zones) are found around hydrogen atoms bound to heteroatoms, highlighting potential sites for electrophilic interactions and hydrogen bond donation. These distributions suggest similar polarity patterns across the conformers, with subtle differences that may influence their intermolecular recognition and reactivity. Among the studied structures, compound **4a** shows the most pronounced spatial separation between donor and acceptor regions.

3.4. DFT-Based Simulation of Electronic Absorption and Luminescence Properties

To elucidate the electronic transitions and photophysical behavior of the studied conformations, we performed TD-DFT calculations of UV-vis absorption spectra and emission luminescence spectra for **4a-II**, **4b-II** and **4c-II'** conformations, aiming to establish structure–property relationships relevant to optoelectronic applications. The calculated absorption and emission spectra are presented in Figure 7.

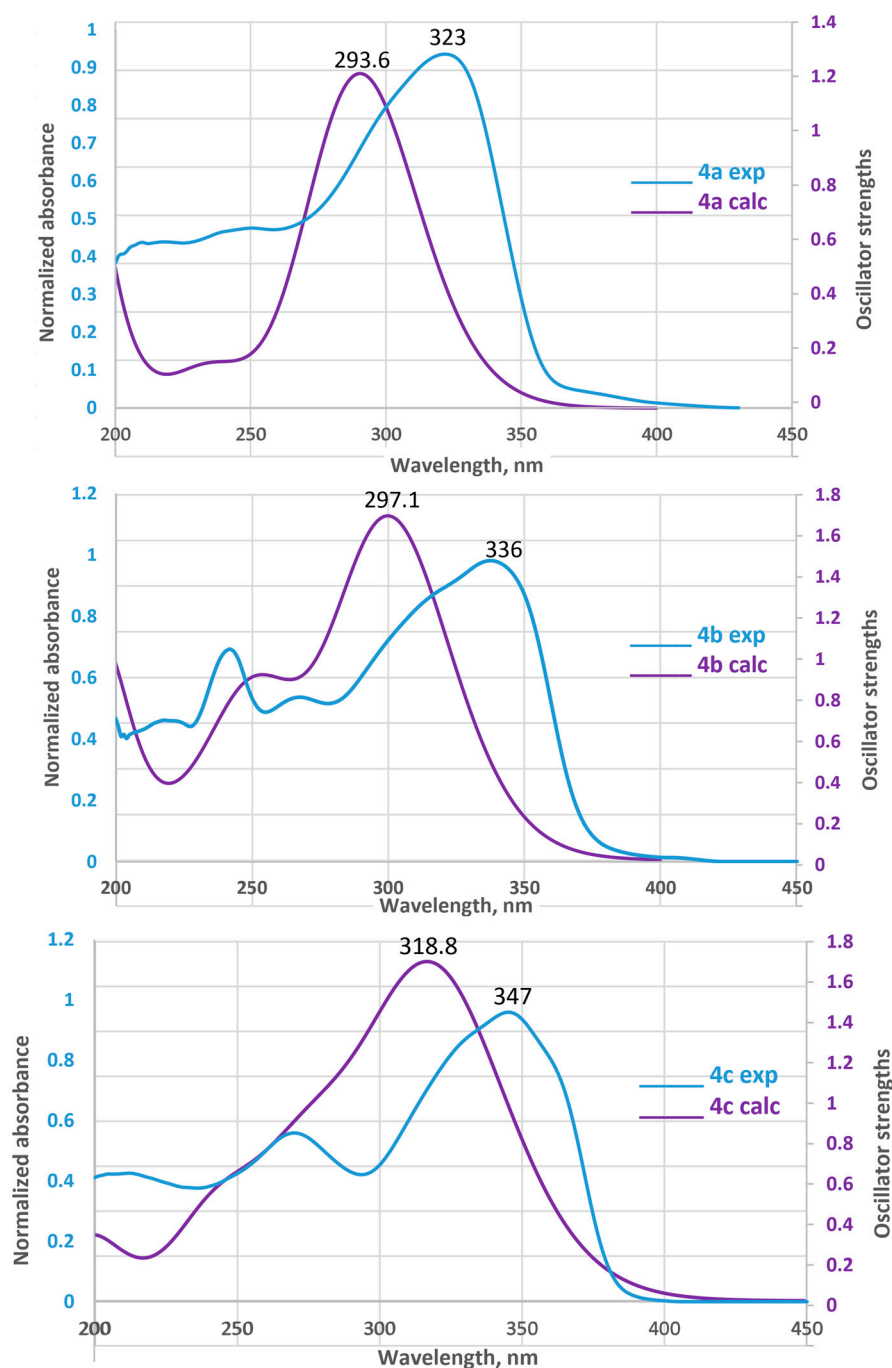


Figure 7. TD-DFT calculated UV-vis absorption spectra in acetonitrile (CH_3CN) for the **4a-II**, **4b-II** and **4c-II'** conformations.

The calculated UV-vis absorption spectra of the **4a-II**, **4b-II** and **4c-II'** conformations exhibit distinct profiles, reflecting differences in their electronic structures and transition energies (Figure 7). All spectra show pronounced absorption bands in the 290–320 nm

range, characteristic of $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ electronic transitions and corresponding to experimental peaks in the range of 323–347 nm. The comparison between the experimental and calculated spectra shows a satisfactory level of agreement: the overall spectral pattern and the positions of the main peaks coincide qualitatively. At the same time, exact quantitative matching is not observed, as the calculated absorption maxima are shifted by 25–40 nm relative to the experimental values. This deviation is expected, since TD-DFT methods are well known to reliably reproduce spectral trends but typically exhibit absolute errors of 0.3–0.5 eV (approximately 25–40 nm), especially for $\pi \rightarrow \pi^*$ transitions [52,53].

The **4a-II** conformation displays the most blue-shifted absorption maximum, located near 293.6 nm, indicating the largest HOMO–LUMO energy gap among the three compounds. The **4b-II** conformation peaks slightly later, around 297.1 nm, with comparable intensity and a narrower band shape, suggesting efficient electronic excitation with minimal structural distortion. In contrast, the **4c-II'** shows the most red-shifted and intense absorption band, centered near 318.8 nm, accompanied by a broader spectral profile. This behavior implies a reduced excitation energy and potentially greater charge delocalization or π -conjugation within the molecular framework. The observed bathochromic shifts and variations in peak intensity correlate with differences in molecular geometry, electronic distribution, and substituent effects.

The simulated emission spectra of the three compounds reveal distinct photophysical behaviors, as illustrated in Figure 8.

As can be seen in Figure 8, the **4a-II** conformation exhibits the most intense and narrow luminescence band, with a maximum at approximately 344.8 nm, indicating the largest energy gap between the first excited singlet state (S_1) and the ground state (S_0) and corresponding to the experimental peak in the 368 nm range. In contrast, the **4b-II** and **4c-II'** conformations display progressively broader and red-shifted emission profiles, with maxima near 382 (experimental peak 382 nm) and 421.2 nm (experimental peak 431 nm), respectively. These spectral shifts suggest a reduction in the S_1 – S_0 energy gap, likely due to conformational relaxation, substituent effects, or enhanced charge delocalization. The observed trend **4a-II** > **4b-II** > **4c-II'** in both peak intensity and energy—correlates with experiment and reflect differences in electronic structure.

Overall, conformation **4a-II** shows the most efficient luminescence, which is likely due to its high molecular symmetry and minimal energy loss from conformational changes. The weaker luminescence observed for conformations **4b-II** and **4c-II'** may result from greater conformational flexibility, intermolecular interactions, or differences in electronic structure. The compound **4a** can be considered a promising candidate for use as a fluorophore or in OLED materials, while **4b** and **4c** are of interest for studying how molecular structure affects spectral properties.

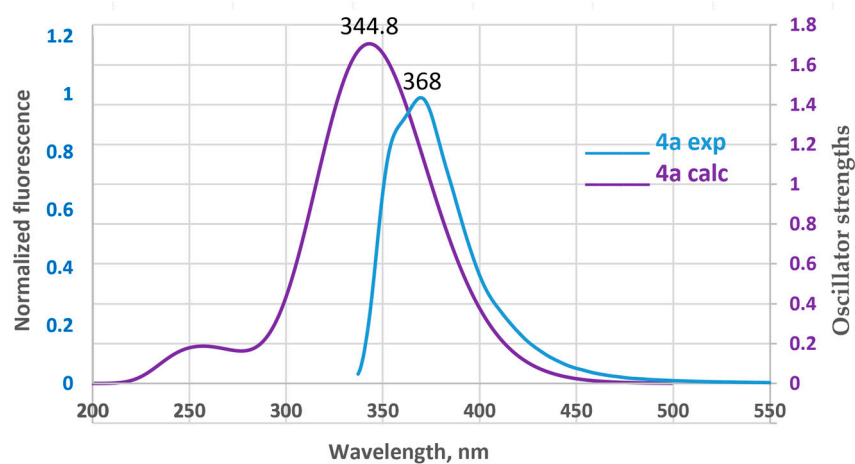


Figure 8. Cont.

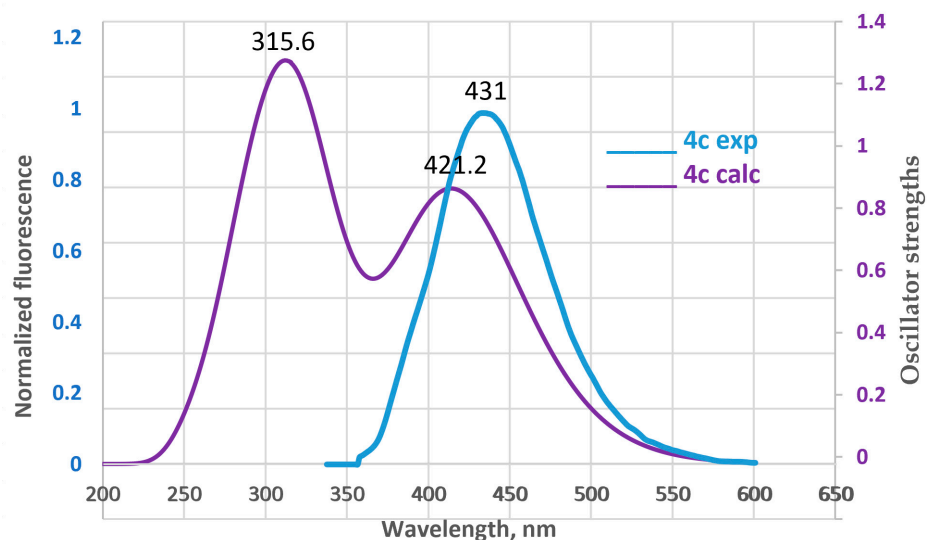
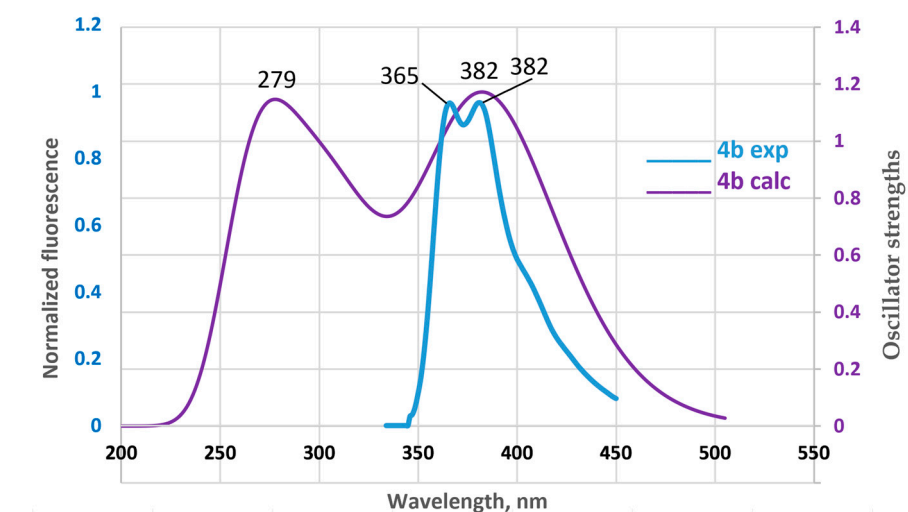


Figure 8. TD-DFT calculated UV-vis emission spectra in acetonitrile (CH_3CN) for the **4a-II**, **4b-II** and **4c-II'** conformations.

4. Conclusions

The aim of this study was to investigate a new group of structurally diverse bis-oxazolo[5,4-b]pyridine derivatives, selected for their close similarity to terpyridines, well-

known ligands in coordination chemistry due to their flexible structure and strong binding capacity. Four new 2,6-bis(oxazolo[5,4-b]pyridin-2-yl)pyridine derivatives **4a–d** were synthesized using our established approach to the cyclization of amide derivatives of 3-aminopyridin-2(1H)-ones, with pyridine-2,6-dicarboxylic acid and its dichloride serving as key acidic components. The newly synthesized compounds were characterized by melting point, HRMS, and ^1H , ^{13}C NMR spectroscopy, and were further examined for photophysical properties (λ_{max} , Stokes shift, quantum yield) in chloroform, dichloromethane, and acetonitrile. It was found that compounds **4a–c** exhibited strong blue or deep blue fluorescence emission in the region 357–474 nm under UV light attributed to π – π^* electronic transitions within the conjugated bis(oxazolo[5,4-b]pyridine) ring system and high fluorescence quantum yields ($\varphi_i \approx 0.32$ – 0.84), highlighting their potential as phosphors for use in organic electronics. Compounds **4a–c** were further examined by DFT ($\omega\text{B97XD/6-311++G(d,p)}$) computational modeling to assess their electronic structure, conformational stability, and photophysical behavior. The analysis revealed that the most stable conformations (**4a–II**, **4b–II** and **4c–II'**) exhibit a decreasing HOMO–LUMO gap and exhibit a progressive decrease in the HOMO–LUMO gap accompanied by enhanced photoactivity from **4a** to **4c**. Among the studied compounds, **4a** can be identified as the most promising luminophore due to its intense and narrow luminescence band, which arises from its high molecular symmetry and stable emission behavior. Future research can focus on expanding the structural diversity of bis(oxazolo[5,4-b]pyridine) derivatives and studying their coordination behavior with metal ions to develop new functional materials for optoelectronic applications.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/compounds6010012/s1>, Copies of ^1H , ^{13}C NMR spectra and Mass spectra; Scheme S1. Detailed conformational landscape of compound **4a**; Scheme S2. Detailed conformational landscape of compound **4b**; Scheme S3. Detailed conformational landscape of compound **4c**; Table S1. Total Electronic Energy (E_{total}) and Gibbs Free Energy (G) of various conformations of compounds **4a–c** in vacuum and in solvents (CH_2Cl_2 , CH_3CN); Table S2. Atomic cartesian coordinates of optimized geometry of **4a–II**; Table S3. Atomic cartesian coordinates of optimized geometry of **4b–II**; Table S4. Atomic cartesian coordinates of optimized geometry of **4c–II'**.

Author Contributions: Conceptualization, methodology, resources, supervision, I.V.K. and I.A.P.; software, I.A.P.; investigation, validation, formal analysis, data curation, I.V.P., S.S.V. and A.S.R.; writing—original draft preparation, writing—review and editing, visualization, I.V.P., I.V.K. and I.A.P.; writing—review and editing, visualization, A.S.N., project administration, funding acquisition, I.V.P. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The original contributions presented in this study are included in the article/Supplementary Material. Further inquiries can be directed to the corresponding authors.

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Conflicts of Interest: The authors declare no conflict of interest.

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