

Article

SYNTHESIS, STRUCTURAL AND PHOTOPHYSICAL PROPERTIES OF A NEW DITOPIC TERPYRIDINE-BASED PROLIGAND BEARING DISELENIDE UNITS

Adelina A. ANDELESCU^{1*}, Evelyn POPA¹, Elisabeta-Ildyko SZERB¹

¹“Coriolan Drăgulescu” Institute of Chemistry, Romanian Academy, 24 Mihai Viteazu Blvd., 300223 Timisoara, Romania

Abstract: The present paper describes the synthesis and characterization of a new ditopic proligand with two terpyridines linked by a diselenide unit, obtained by a Steglich esterification procedure between a biscalboxylic acid functionalized with a diselenide unit and 4-([2,2':6',2''-terpyridin]-4'-yl)phenol. The compound was characterized by FT-IR, NMR (1D and 2D) and UV-Vis spectroscopies and ESI-MS analysis. Moreover, the photophysical properties of the ditopic ligand were investigated in freshly prepared dichloromethane solution. The compound was found to be emissive with a maximum centered at 354 nm.

Keywords: heterocycles; N-donor ligand; ditopic ligand; oligopyridines;

INTRODUCTION

The molecule 2,2':6',2''-terpyridine (*tpy*) is a tridentate ligand with three nitrogen coordination sites (Mughal et al. 2020) and was first reported in 1932 by Morgan and Burstall as one of 20 products of the reaction when they heated pyridine and anhydrous iron(III) chloride in an autoclave (Morgan and Burstall 1932).

Since then, *tpy* and its derivatives have received attention due to their ability to easily form metal complexes with main-group, *d*-block and lanthanide elements (Fallahpour 2002, Mughal et al. 2020). *Tpy* derivatives and their metal complexes have been studied in supramolecular chemistry and catalysis (Wey et al. 2019), electrochemical sensors (Negrea et al. 2022, Popa et al. 2023), as DNA binders and medicinal chemistry (Abhijnakrishna et al. 2023), etc.

Various synthetic procedures have been employed for the synthesis of *tpy* scaffolds (Fallahpour 2002, Kainat et al. 2024), such as cross-coupling [Li et al. 2011, Robo et al. 2014, Zibaseresht 2019] or ring assembly methods (Fernandes et al. 2018, Wang et al. 2019).

Among them, the one-pot Kröhnke reaction [Kröhnke 1976] is the most commonly employed method, and it involves the reaction of two equivalents of a substituted acetylpyridine derivative with an aldehyde in a basic medium and in the presence of an ammonia source. Following the Kröhnke

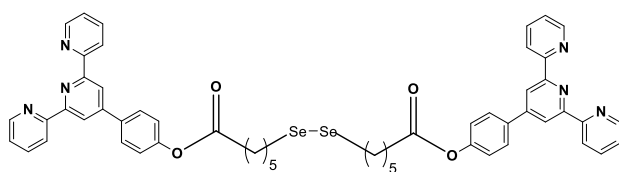
methodology, a wide variety of 4'-substituted *tpy* derivatives were reported (Kainat et al. 2024).

Ditopic ligands, with two different, separated metal-binding domains in their structures, can form two types of coordination compounds: homo and hetero multi-metallic complexes (Salimova et al. 2020, Schäfer et al. 2021)

The first of these are complexes in which both ligand fragments, coordinate the same metal ion. Polymetallic complexes may be obtained using ditopic terpyridinyl units resulting in luminescent materials or electrochemical sensors [Indelli et al. 1998, Andeleescu et al. 2024].

Moreover, the synthesis of ditopic *tpy* derivatives with an additional donor atom (such as: sulphur or selenium) is of interest due to their ability to bind nanoparticles (Yee et al. 2003, Rudakovskaya et al. 2010, Romashkina et al. 2013, Margandan et al. 2017, Popa et al. 2024). On this background, we report the synthesis and characterization of a new ditopic *tpy* proligand, namely bis(4-([2,2':6',2''-terpyridin]-4'-yl)phenyl)6,6'-diselanediyldihexanoate (Figure 1), which contains additionally an aromatic ring on its structure, compared to the one previously reported by our group (Popa et al. 2024). Also, the insertion of selenium atom into the structure may lead to compounds with potential applications as drugs (Banerjee et al. 2017). Due

to the presence of three nitrogen rings, the ditopic terpyridine-based ligand may find future applications as coordination polymers (Shu *et al.* 2022), whereas the presence of a diselenide unit enables them to be studied as drug delivery systems or anticancer drugs (Han *et al.* 2019). The compound was structurally characterized by FT-IR, NMR, and UV-Vis spectroscopies. The proposed structure is supported by the ESI-MS analysis. The photophysical properties of the final compound were investigated in freshly prepared dichloromethane solution.



Compound 3

Figure 1. Proposed chemical structure of the terpyridine derivative.

MATERIALS AND METHODS

N,N' -dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (4-DMAP), 2-acetylpyridine, 4-methoxybenzaldehyde, anhydrous THF, and DMF were purchased from Sigma Aldrich and used without any further purification. The solvents used for the column chromatography were purchased from Carlo Erba. Neutral Al_2O_3 60 and spectrofluorimetric grade dichloromethane were purchased from VWR.

Melting point was determined by optical microscopy using an Olympus BX53M polarizing microscope (POM) equipped with a Linkam hot-stage. Infrared spectra (KBr pellets) in the range 4000-400 cm^{-1} range were recorded on a Cary 630 FT-IR spectrophotometer.

The 1H -NMR spectra were recorded either on a Bruker Fourier 300 MHz spectrometer or Bruker Avance 300) in $CDCl_3$ or $DMSO-d_6$. 1D and 2D NMR experiments were recorded on Bruker Avance III HD – 500 MHz spectrometer in $CDCl_3$.

Spectrofluorimetric grade dichloromethane was used for the photophysical investigations in solution. The absorption spectrum in solution was recorded on an Agilent Cary 60 spectrophotometer using quartz cuvettes of 1 cm path length. The emission spectrum were

recorded on Horiba Fluoromax Plus spectrofluorometer. The luminescence quantum yields of the samples in the solution were recorded using a QuantaPhi-2 integrating sphere with 121 mm internal diameter with reflectivity from 250 to 2500 nm.

High-resolution mass spectral (HRMS) spectra was recorded on Orbitrap IQ-X Mass Spectrometer from Thermo Scientific using an electrospray ionization (ESI) technique. The equipment was operated in positive-ion mode and ion transfer parameters were optimized to enable detection of ions in a m/z range between 150 and 2000. The employed parameters are listed in Table 1. The system was externally calibrated by using Pierce FlexMix Calibration Solution from Thermo Scientific. The data was collected in positive MS scan mode and processed using Thermo Scientific Xcalibur 4.7 software.

Table 1. Employed parameters for ESI-MS technique

Source parameters	Values
Ionization mode	Positive electrospray ionization
Spray voltage	3200 V
Sheath gas flow rate	5 Arb
Auxiliary gas flow rate	2 Arb
Sweep gas flow rate	0 Arb
Ion transfer tube temperature	300 °C
Vaporizer temperature	20 °C
Acquisition parameters	Values
Detector type	Orbitrap
Orbitrap resolution	120000
Scan range	400-1500 m/z
AGC target	100%
Injection time	100 ms
Syringe flow	5 μ l/min

EXPERIMENTAL SECTION

Synthesis of 4-([2,2':6',2''-terpyridin]-4'-yl)phenol, 2

Compound 2 was obtained in two steps following a reported procedure (Bahrami *et al.* 2017) and the results agree well with the reported data.

I1: white solid (0.91 g, 2.68 mmol, 65.6 %).

FT-IR (KBr, cm^{-1}): 2992 (ν (C-H)); 1600 – 1431 (ν (C=N)) and (ν (C=C)).

1H -NMR (300 MHz, $CDCl_3$, δ /ppm): 8.75 - 8.59 (m, 6H), 7.94-7.68 (m, 4H), 7.42-7.25 (m, 2H), 7.12-6.92 (m, 2H), 3.89 (s, 3H);

Compound **2**: pale grey solid (0.720 g, 2.21 mmol, 93 %).

FT-IR (KBr, cm^{-1}): 3250 (ν_{OH} , broad); 1616 – 1430 (ν (C=N)) and (ν (C=C)).

$^1\text{H-NMR}$ (300 MHz, DMSO- d_6 , δ/ppm): 8.77-8.70 (d, 2H), 8.69-8.55(d, 4H), 8.07- 7.95 (td, 2H), 7.81 -7.60(m, 2H), 7.57- 7.43 (m, 2H), 7.00- 6.95(dd, 2H).

*Synthesis of bis(4-([2,2':6',2''-terpyridin]-4'-yl)phenyl) 6,6'-diselanediyldihexanoate, **3***

0.09 g (0.23 mmol) of compound **1**, 0.166 g (0.51 mmol) of compound **2** and 22.65 mg (0.1854 mmol) of 4-DMAP in 10 mL THF and 1 mL of DMF were stirred at room temperature under argon atmosphere for 30 minutes, then 0.105 g (0.51 mmol) of DCC in 3 mL of THF were added dropwise. The consumption of the starting materials was monitored on TLC (Al_2O_3 : CHCl_3 :hexane = 1:1). After 5 days, the reaction mixture was taken to dryness, dissolved in CHCl_3 , washed with distilled water (3x50 mL), the organic phase was dried over anhydrous sodium sulfate, filtered and taken to dryness. The residue was taken with AcOEt and the undissolved precipitate was filtered (to remove the DCU biproduct) and mother liquor was taken to dryness. This procedure was repeated 3 times. The pure compound was isolated after purification on column chromatography using Al_2O_3 as stationary phase in CHCl_3 :hexane = 1:1, resulting in a yellow gel (0.058 mmol, 25%).

Melting point: 83-85°C.

FT-IR (KBr, cm^{-1}): 1762 ($\nu_{\text{C=O}}$); 1605 – 1412 (ν (C=N)) and (ν (C=C)).

$^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ/ppm): 8.67 – 8.62 (m, 4H), 8.58 (dt, $J = 7.9, 1.1$ Hz, 2H), 7.86 – 7.82 (m, 2H), 7.80 (td, $J = 7.7, 1.8$ Hz, 2H), 7.27 (ddd, $J = 7.5, 4.8, 1.3$ Hz, 2H), 7.18 – 7.15 (m, 2H), 2.90 (t, $J = 7.4$ Hz, 2H), 2.55 (t, $J = 7.4$ Hz, 2H), 1.81 – 1.71 (m, 4H), 1.50 (tdd, $J = 9.9, 8.6, 5.1$ Hz, 2H).

$^{13}\text{C-NMR}$ (126 MHz, CDCl_3 , δ/ppm) δ 171.88, 156.07, 155.88, 151.49, 149.38, 149.06, 136.99,

136.02, 128.46, 123.90, 122.11, 121.43, 118.83, 34.27, 30.60, 29.68, 28.92, 24.41.

HR-MS ($\text{C}_{54}\text{H}_{48}\text{N}_6\text{O}_4\text{Se}_2+\text{H}$): simulated: 1005.21442, found: 1005.21402

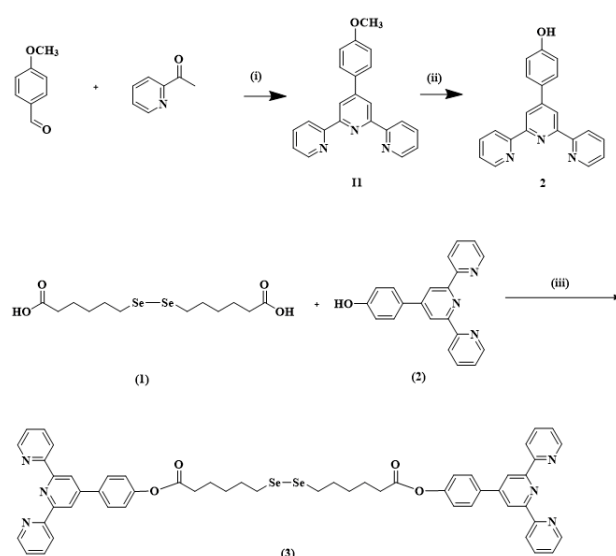
RESULTS AND DISCUSSIONS

The preparation of compound **3**, required the synthesis of the starting materials: 6,6'-(1,2-diselanediyldihexanoic acid, **1** and 4-([2,2':6',2''-terpyridin]-4'-yl)phenol, **2**.

6,6'-(1,2-diselanediyldihexanoic acid, **1** was obtained and fully characterized in a previously published paper of our group [Popa *et al.* 2024].

For the synthesis of 4-([2,2':6',2''-terpyridin]-4'-yl)phenol, **2** a reported procedure was followed, which involved a one-pot Kröhnke condensation between 4-methoxybenzaldehyde and 2-acetylpyridine, in a basic media [Bahrami *et al.* 2017]. The pure compound was isolated after a recrystallization from methanol [Chen *et al.* 2018]. The intermediate **11** was then demethylated under strong acidic conditions to yield the desired compound **2**. The reaction pathway is presented in Scheme 1.

The desired compound **3**, bis(4-([2,2':6',2''-terpyridin]-4'-yl)phenyl) 6,6'-diselanediyldihexanoate was obtained adapting a procedure reported by our group (Scheme 1, Popa *et al.* 2024), through a Steglich esterification reaction between compound **1** and **2** equivalents of compound **2**, using DCC as a coupling reagent in the presence of 4-DMAP as catalyst.



Scheme 1. Reaction pathway for the synthesis of compounds **2** and **3**. Reagents and conditions: (i) KOH, EtOH, NH₄OH, Δ T, 24 hours; (iii) DCC, 4-DMAP, THF-DMF (10-1 V/V), inert atmosphere, r.t, 5 days;

Compound **3** was isolated as a yellow waxy solid. Its structure was proposed based on spectroscopic methods: FT-IR, NMR (1D and 2D) spectroscopy and MS spectrometry.

The first confirmation of the formation of the desired compound **3**, was gained from FT-IR analysis through the shift of the characteristic absorption band of the carbonyl group ($\nu_{C=O}$) from 1694 cm⁻¹ in compound **1**, to 1762 cm⁻¹ in compound **3**, which is characteristic of the C=O bond in esters. Moreover, the stretching vibration of the ν_{C-Se} bond is identified at 635 cm⁻¹ in compound **1**, and 640 cm⁻¹ in compound **3** (Helios et al. 2015). The main characteristic absorption bands of the compound are reported in Table 2.

Table 2. Assignment of the characteristic absorption bands of the starting materials and the final compound **3**.

Cpd	Assignment of the characteristic absorption bands (wavenumber values in cm ⁻¹)		
	$\nu_{C=O}$	$\nu_{C=N \text{ and } C=C}$	ν_{C-Se}
1*	1694	-	635
2	-	1616 – 1430	-
3	1762	1605 – 1412	641

* Data reported in Popa *et al.* 2024

In order to confirm the proposed structure, 1D and 2D NMR spectra were recorded on a Bruker 500 MHz instrument. This allowed us to fully index all the protons and carbon atoms based on ¹H-¹H COSY (Correlation Spectroscopy), HSQC (Heteronuclear Single Quantum Coherence), and HMBC (Heteronuclear Multiple Bond Correlation) experiments. The results are summarized in Table 3.

Table 3. 1D and 2D NMR data of compound **3** recorded in CDCl₃

Atom label	¹ H	¹³ C	COSY	HMBC
C	1.50 (tdd, $J = 9.9, 8.6, 5.1$ Hz, 2H)	28.92	B,D	A, D, E
B, D	1.81 – 1.68, m, 4H	30.60 (B), 24.41 (D)	A,E,C	A, D, E, F,

E	2.55, t, $J = 7.4$ Hz, 2H	34.27	D	D,C,F
A	2.90 (t, $J = 7.4$ Hz, 2H),	29.68	B	-
F	-	171.88	-	-
1*	8.67 – 8.62 (m, 4H)	149.06	2	2, 3
2	7.27 (ddd, $J = m, 2H$)	123.90	1, 3	1, 4, 5, 6
3	7.80 (td, $J = 7.7, 1.8$ Hz, 2H)	136.99	1, 2	1, 4, 6
4	8.58 (dt, $J = 7.9, 1.1$ Hz, 2H)	121.43	3	2, 5, 6
5	-	155.88	-	-
6	-	156.07	-	-
7*	8.67 – 8.62 (m, 4H)	118.83	-	4, 5, 6, 9, 11,
8	-	149.38	-	-
9	-	136.02	-	-
10	7.86 – 7.82 (m, 2H)	128.46	11	8, 11, 12
11	7.23 – 7.08 (m, 2H)	122.11	10	9, 12
12	-	151.49	-	-

* Peaks appear overlapped in ¹H-NMR spectra in total 4H

The ¹H-NMR spectrum (Figure 2) presented all the expected signals of the protons, and their integration agrees with the proposed structure, while the ¹³C-NMR spectra contained all the expected signals for the 18 carbon atoms from half of the molecule.

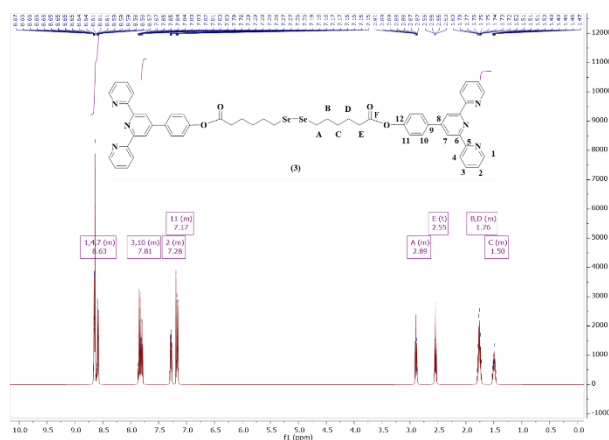


Figure 2. The ¹H-NMR spectrum of compound **3** recorded in CDCl₃ and the atom labeling.

Finally, the proposed structure is supported by the ESI-MS analysis (Figure 3).

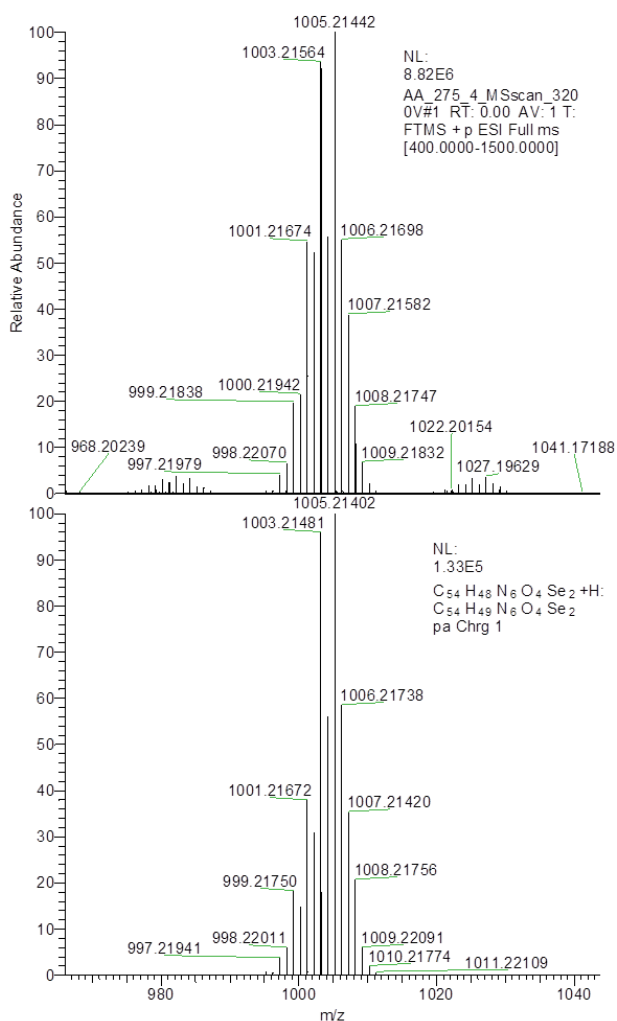


Figure 3. Simulation vs. experimental MS spectra for compound 3.

The photophysical properties of compound 3 (absorption, emission maxima and lifetimes of the excited states) were determined in freshly prepared dichloromethane solution and the data are presented in Figure 4 and summarized in Table 4. From the absorption spectra several information could be obtained: the absorptions band from 252 and 280 nm are due to π - π^* from the *tpy* ring (Toledo *et al.* 2015), whereas the shoulder centered at 311 nm may be due to the diselenide bond (Back *et al.* 1983). It is well known that the *tpy* scaffolds present fluorescence properties at room temperature (Costa *et al.* 2015), therefore the emission spectrum was recorded after excitation at 311 nm, presenting an emission band centered 354 nm.

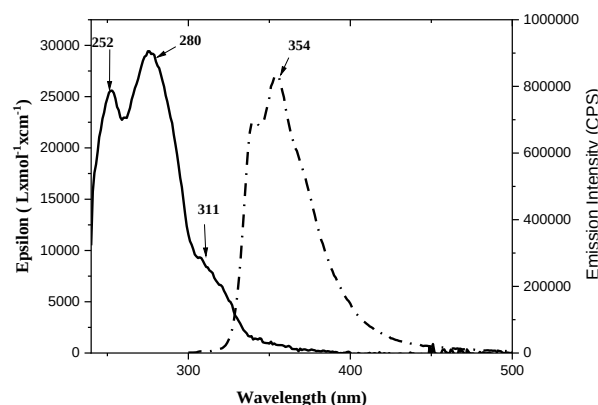


Figure 4. Absorption (solid line) and emission (dashed line) of compound 3 in CH_2Cl_2 solution ($c= 5 \cdot 10^{-6}$ mol/L).

Table 4. Photophysical properties of compound 3 in solution ($c= 5 \cdot 10^{-6}$ mol/L).

Sample	Abs, $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$)	Em, $\lambda_{\text{max}}/\text{nm}$	ϕ /%
1*	308 (640)	-	-
2**	286, 330-410	384	-
3	252 (25512) 280 (29364) 311 (9077)	354 ($\lambda_{\text{ex}}=311$ nm)	6.33

* Data reported by Popa *et al.* 2024

** Data recorded in ethanol solution reported by Sierra *et al.* 2018

Structurally similar terpyridine ligands with disulfide moieties were reported by Majouga *et al.* 2010, but their photophysical properties were not investigated, whereas in case of those with diselenide units, there is only one reported by our group (Popa *et al.* 2024) with its emission maxima centered at 349 nm. Compared to the compound reported in the present paper it presents a small bathochromic shift of 5 nm. The compound presented a quantum yield value of 6.33 %.

Recently it was mentioned that linear diselenides quenched fluorescence through a synergistic combination of intramolecular charge transfer, ICT and Förster resonance energy transfer, FRET (Ma *et al.* 2024). Therefore, the low quantum yield value may be attributed to the quenching effect of the diselenide moiety.

CONCLUSIONS

A new terpyridine derivative containing a diselenide unit was obtained and its structure was confirmed based on FT-IR, NMR (1D and

2D) investigations and HR-MS spectrometry. Its optical properties were investigated in freshly prepared dichloromethane solutions by UV-Vis and fluorescence measurements.

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