Scientific Research Publishing

Spectral Analysis Reviews, 2025, 8(1), 1-15
https://www.scirp.org/journal/sar
ISSN Online: 2331-2106
ISSN Print: 2331-2092

Theoretical Study of the Spectroscopic Properties of a Series of Makaluvamines in the Ultra-Violet Visible Range Using DFT (B3LYP) and TD-DFT Methods

Atse Adepo Jacques[1], Diomande Sékou[2], Alao Latifatou Laye[1], Kone Soleymane[1*]

[1]Laboratory of Constitution and Reaction of Matter, UFR SSMT, University Felix Houphouët Boigny, Abidjan, Côte d'Ivoire
[2]Department of Agro-Industrial Sciences and Technologies (STAgI), UFR Agriculture, Halieutic Resources and Agro-Industry, University of San-Pédro, San-Pédro, Côte d'Ivoire
Email: *konesol2003@yahoo.fr

How to cite this paper: Jacques, A.A., Sékou, D., Laye, A.L. and Soleymane, K. (2025) Theoretical Study of the Spectroscopic Properties of a Series of Makaluvamines in the Ultra-Violet Visible Range Using DFT (B3LYP) and TD-DFT Methods. *Spectral Analysis Reviews*, **8**, 1-15.
https://doi.org/10.4236/sar.2025.81001

Received: August 30, 2024
Accepted: January 4, 2025
Published: January 7, 2025

Abstract

This work was carried out with the aim of contributing to the treatment of cancer. Cancer is one of the most common causes of death. It constitutes a public health problem. Photodynamic therapy (PDT) is one treatment option. This study contributes to the search for photosensitizing molecules used in PDT. Makaluvamines have shown interesting properties in the treatment of several human cancer cell lines. The present study analyzes the ultraviolet and visible absorption spectroscopic properties of a few Makaluvamines. These have been listed in the literature and can be in neutral or charged states (protonated and methylated). The investigation is based on quantum chemical calculations. Molecular geometries and vibrational frequencies have been calculated at the B3LYP/6-311++G(d,p) level. Absorption properties in the visible and ultraviolet spectral range are measured on optimized structures using time-dependent density functional theory (TD-DFT). The absorption spectra are obtained using the "Chemissian" software. The results of our calculations have allowed us to determine the absorption zones of the molecules studied, the energy gaps of the frontier orbitals, the main transitions associated with the absorption process, and their lifetimes. They have also identified four Makaluvamines (E, G, M, and L) that absorb in the therapeutic domain and may have photosensitizer properties.

Keywords

Cancer, Makaluvamines, Density Functional Theory, Time-Dependent Density Functional Theory, Photosensitizer, Absorption

1. Introduction

In some countries, cancer is the main cause of death, ahead of cardiovascular disease [1]. It is a pathology that is widespread throughout the world. It represents a real public health problem. Consequently, its treatment is a hot topic for scientific research. These include the development of treatments with fewer side effects. Photodynamic therapy (PDT) is one of the treatments available today. This is a technique whose biophysical principles were experimentally established over 100 years ago by Raab O. and Tappeiner HV [2] [3]. This technique consists of sensitizing carcinoid cells to the action of light (photon) by prior injection of a photosensitizing molecule that is preferentially captured and retained in cancerous tumors. In 1978, Dougherty made the first applications in digestive oncology with Hematoporphyrin Derivative (HpD) [4]. Because of the anti-carcinoid properties of Makaluvamines [5] [6], In our opinion, this work is the very first to study the photosensitizing activity of a series of these molecules. Specifically, it studies the absorption properties of a series of these molecules in the visible and ultraviolet range. A molecule with good photosensitizing properties must absorb in the therapeutic visible range [7]. This work is a theoretical study carried out using quantum chemical computational methods, such as Density Functional Theory (DFT) and Time-Dependent DFT (TD-DFT). DFT calculations are increasingly used in spectroscopy to verify certain properties or structures of molecules [8] [9]. First, DFT is used to calculate the molecular geometries of the Makaluvamines series and their vibrational frequencies. The absorption properties in the UV-visible spectral range are then calculated using the optimized structures. These are performed using the TD-DFT method. Finally, the absorption spectra are obtained using "Chemissian" software. For each molecule in the series, the absorption spectrum, absorption bandwidth, maximum absorption wavelength, energy gap of the frontier orbitals, main electronic transition, and lifetime are determined.

2. Studied Molecules and Calculation Methods

2.1. Studied Molecules

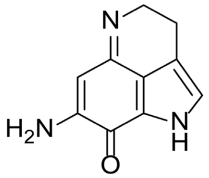
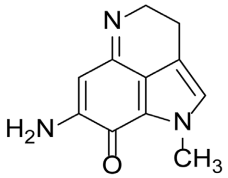
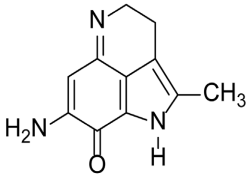
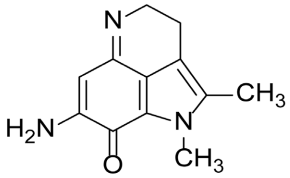
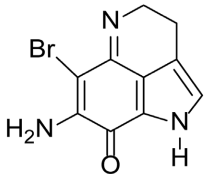
The studied molecules are listed in **Figure 1** below. They have been listed in the literature with refcodes corresponding to letters of the alphabet. These molecules exist in the literature in two forms, either neutral or charged.

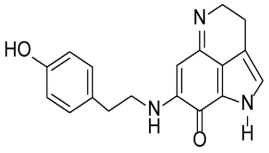
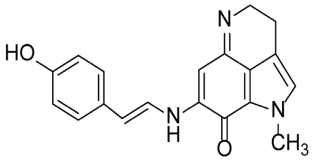
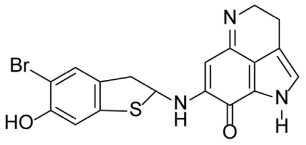
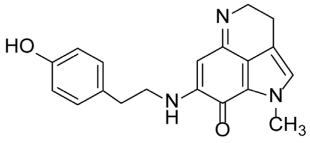
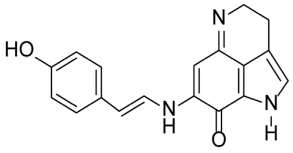
Makaluvamine I (**Figure 2**), named according to the systematic nomenclature 7-amino-2a1, 3, 4, 8a-tetrahydropyrrolo [4,3,2-de] quinone 8 (1H)-one, is chosen as the structural reference. It carries no substituents and is neutral in the literature. This skeleton forms the structural basis of Makaluvamines.

For this study, we considered the neutral and charged (protonated then methylated) forms for each Makaluvamine. The following notations are therefore adopted: X (neutral), XH+ (protonated) and XMet (methylated). The Makaluvamines in the series under study are grouped into so-called clusters. These groups, of which there are 4, contain molecules with strong structural similarities.

***Group* 1** is made up of molecules A, C and H. These have a methyl substituent

on either atom 1 or 2 of the pyrrolic ring (A and C), or on both (H).

Makaluvamine	Refcode/nature
	I / Neutral A_1 / methylated
	A / Neutral
	C / Neutral
	H / Neutral
	N / Neutral

Makaluvamine	Refcode/nature
	D / Protonated J / methylated
	E / Protonated G / methylated
	F / Protonated
	K / Protonated P / methylated
	M / Protonated L / methylated

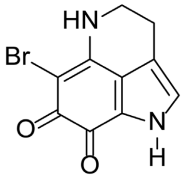
Makaluvamine	Refcode/nature
	O / Neutral

Figure 1. 2D structures of the various studied Makaluvamines.

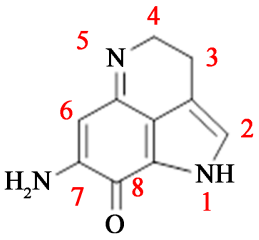


Figure 2. Makaluvamine I is a structural reference in the studied series.

***Group* 2** contains Makaluvamines D/J, F, M/L and V. In these molecules, hydrogen on the amino nitrogen (N_7) is replaced by a strongly electron-conjugated substituent.

***Group* 3** includes Makaluvamines E/G and K/P. They are distinguished by the presence of two substituents. One is a methyl substituent on the pyrrole nitrogen, and the other is a strongly electron-conjugated substituent on the amino nitrogen. Each compound in this group has the characteristics of a Group 2 compound and

a ***Group* 1** compound A.

***Group* 4** contains Makaluvamines N and O. These molecules are obtained by substitutions in positions 6 and 7 on the pyridine ring of the basic structure.

It's important to note that these groups are defined regardless of the neutral or charged (protonated or methylated) nature of the pyridine nitrogen (N^5).

2.2. Calculation Methods

Calculations are performed using Gaussian 09 software [10]. The methods used are Density Functional Theory (DFT) [11] and Time-Dependent Density Functional theory (TD-DFT) [12]-[14]. These choices are justified by the fact that hybrid functionals such as B3LYP and others, combined with a wide base of functions, lead to values in good agreement with experimental results [15]. TD-DFT is a generalization of the density functional formalism for determining electronic excitation absorption spectra [16]. The B3LYP/6-311++G(d,p) level of theory was used for optimization calculations of the molecular geometry and vibrational frequencies of the Makaluvamines in the studied series. The TD-DFT method was used to calculate absorption properties, with a single point for each structure optimized at the B3LYP/6-311++G(d,p) level. "Chemissian" software was used to produce the spectra.

For a molecule, the excited state corresponds to the temporary displacement of an electron from the fundamental layer to a higher level. This is observed after the absorption of a photon by the atom or molecule. The lifetime of the excited state is measured according to the following Equation (1) [17].

$$\tau = \frac{1499}{fE^2} \tag{1}$$

with f and E representing the oscillation force of the transition and the wave number in cm^{-1}, respectively.

These various calculations have allowed us to determine the absorption spectra, the absorption bands, the maximum absorption wavelengths, the energy gaps of the frontier orbitals, the main electronic transitions, and the lifetimes of the Makaluvamines in the studied series.

3. Results and Discussion

The results of the spectroscopic parameters calculated for the molecules in each group are compared with those of the reference Makaluvamine I. The neutral forms are compared with each other, and the charged forms (protonated on the one hand and methylated on the other) with each other.

3.1. Comparison of Spectroscopic Parameters of Group 1 Makaluvamines and the Reference

The UV-visible absorption spectra of the I, A, C, and H molecules (a); IH^+, AH^+, CH^+ and HH^+ (b) and IMet, AMet, CMet and HMet (c) are shown in **Figure 3**.

The absorption ranges of Group 1 Makaluvamines, and the reference superpose each other in the visible UV. The absorption bands of the neutral forms (**Figure 3(a)**)

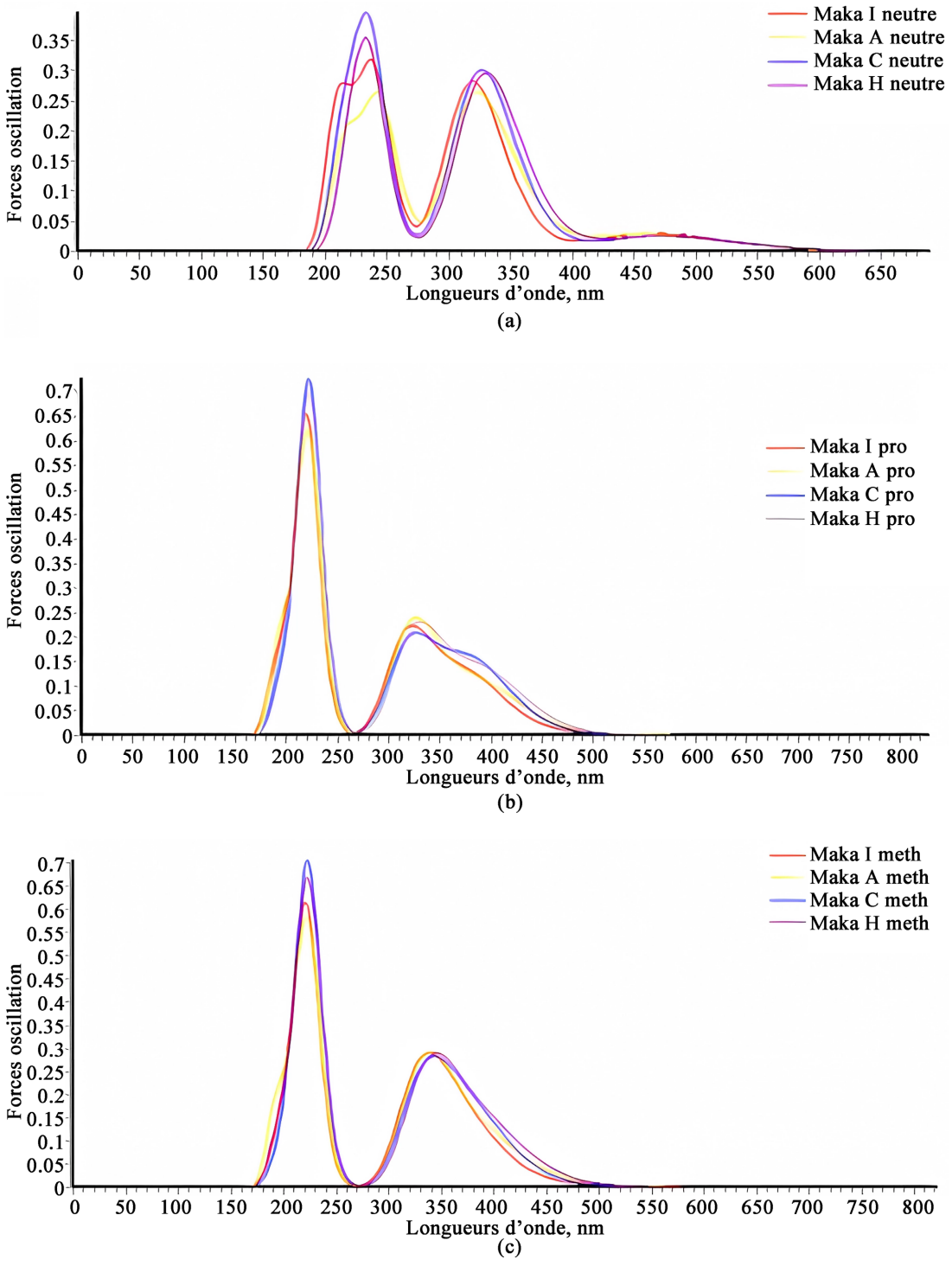


Figure 3. UV visible absorption spectra of Group 1 makaluvamines compared with the reference molecule. (a) Neutral makaluvamines; I, A, C and H; (b) Protonated makaluvamines; IH^+, AH^+, CH^+ and HH^+; (c) Methylated makaluvamines; IMet, AMet, CMet and HMet.

extend from 180 to 600 nm. In their protonated IH^+ and methylated IMet forms, the absorption range of these molecules is reduced from 170 to 480 nm. All these Makaluvamines have two absorption maxima. The two peaks of the reference

Makaluvamine I have almost equivalent intensities. Those of the absorption bands of the charged forms IH+ and IMet are distinctly different. The former is much more intense than the latter. The spectra of group 1 Makaluvamines show similar patterns. The results indicate that protonation or methylation modifies the absorption intensity of these Makaluvamines in the UV visible range. The intensity of the first absorption maximum is at least twice that of the second. For these four molecules, the main electronic transitions among those generated with TD-DFT calculations, the wavelength values of the absorption maxima, the energy gaps between the transition levels, and the lifetime (τ) of the transition [18] are grouped together in **Table 1**.

Table 1. Energy gap (eV), maximum wavelength (nm), lifetimes of main transitions (ns) for Makaluvamines I and Group 1.

Molecules	ΔE	λ_{max}	τ	Principal transition
I	3.22	238.7	33.03	HOMO → $LUMO_{+2}$ (89%)
A	3.23	320.1	66.52	$HOMO_{-1}$ → LUMO (90%)
C	3.21	236.3	32.54	HOMO → $LUMO_{+3}$ (71%)
H	3.21	235.7	32.04	HOMO → $LUMO_{+3}$ (84%)
IH^+	3.11	220.8	12.74	HOMO → $LUMO_{+1}$ (91%)
AH^+	3.12	222.6	18.92	HOMO → $LUMO_{+1}$ (85%)
CH^+	2.97	224.2	13.27	HOMO → $LUMO_{+1}$ (89%)
HH^+	2.97	225.9	18.50	HOMO → $LUMO_{+1}$ (81%)
IMet	3.11	222.5	14.19	HOMO → $LUMO_{+1}$ (87%)
AMet	3.12	224.0	20.33	HOMO → $LUMO_{+1}$ (89%)
CMet	2.97	225.2	14.41	HOMO → $LUMO_{+1}$ (90%)
HMet	2.97	227.0	22.02	HOMO → $LUMO_{+1}$ (78%)

Absorption wavelengths λ_{max} are between 220 nm and 320 nm, *i.e.*, in the ultra-violet range. In the neutral forms of these four molecules, the principal electronic transitions associated with absorption are between HOMO and $LUMO_{+2}$ for Makaluvamine I, and HOMO and $LUMO_{+3}$ for Makaluvamines C and H. As for Makaluvamine A, this transition takes place between $HOMO_{-1}$ and LUMO. When these Makaluvamines are charged, these electronic transitions involve HOMO and $LUMO_{+1}$. This observation indicates that protonation and methylation modify the lowest unoccupied orbital involved in the electronic transitions observed during the absorption of these molecules. Wavelengths located in the Ultra-Violet show that the corresponding transitions are of the $\pi \rightarrow \pi^*$ type [19]-[21]. Transition lifetimes range from 12.74 ns to 66.52 ns. Generally speaking, the charged forms of Makaluvamines have the shortest electronic transition lifetimes.

A short excited state lifetime is favorable to fluorescence. A longer lifetime

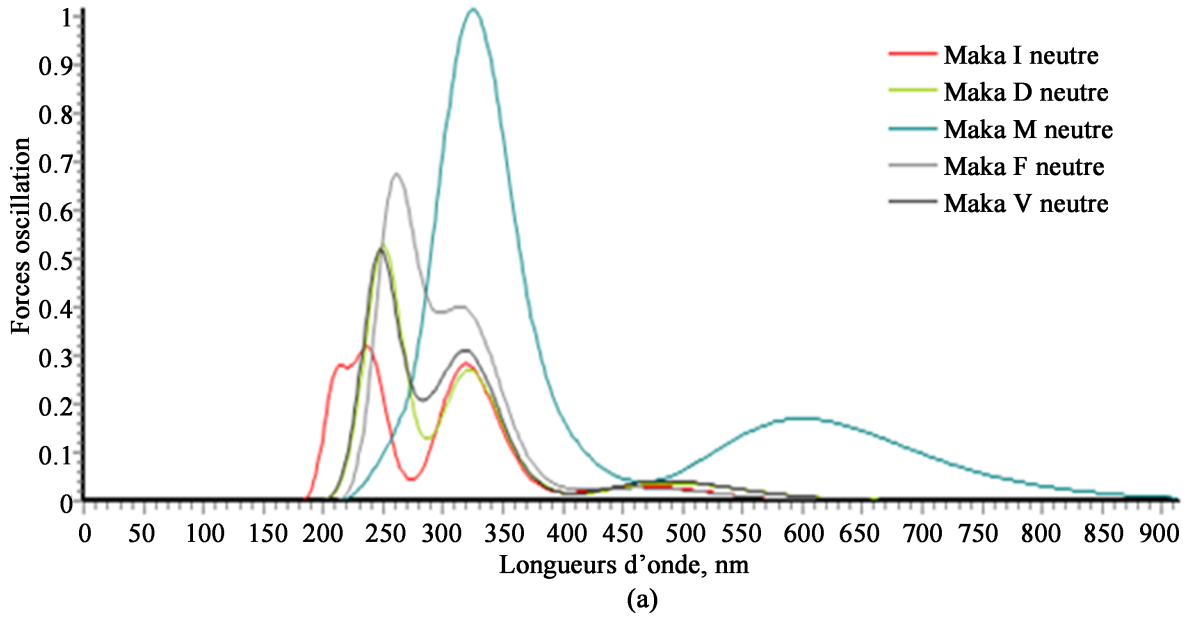
could lead to competition between fluorescence and other photophysical processes. This reflects greater fluorescence activity and relatively minimizes other forms of energy conversion [22].

The energy gaps of these compounds are relatively close. The lowest values are obtained with the charged (protonated and methylated) forms of Makaluvamines. Border orbitals are, therefore, closer together. These results suggest that it is in these forms that the molecules are more reactive.

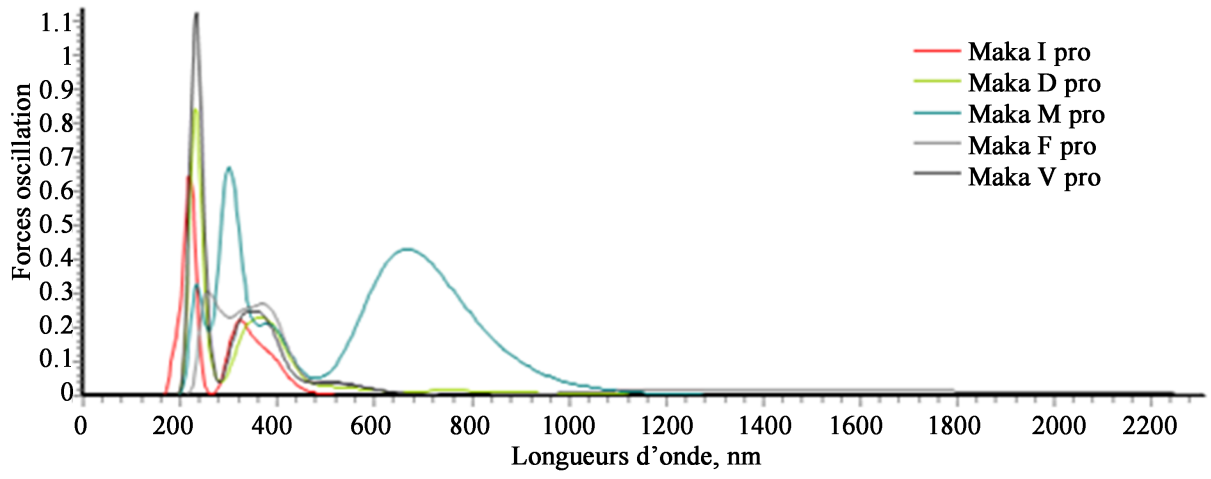
3.2. Comparison of Spectroscopic Parameters of Group 2 Makaluvamines and the Reference

The UV-visible absorption spectra of Makaluvamines I, D, M, F, and V (a); IH^+, DH^+, MH^+, FH^+, and VH^+ (b) then IMet, DMet, LMet, FMet and VMet (c) are grouped together in **Figure 4**.

Figure 4(a) shows that absorption occurs between 180 nm and 600 nm for



(a)



(b)

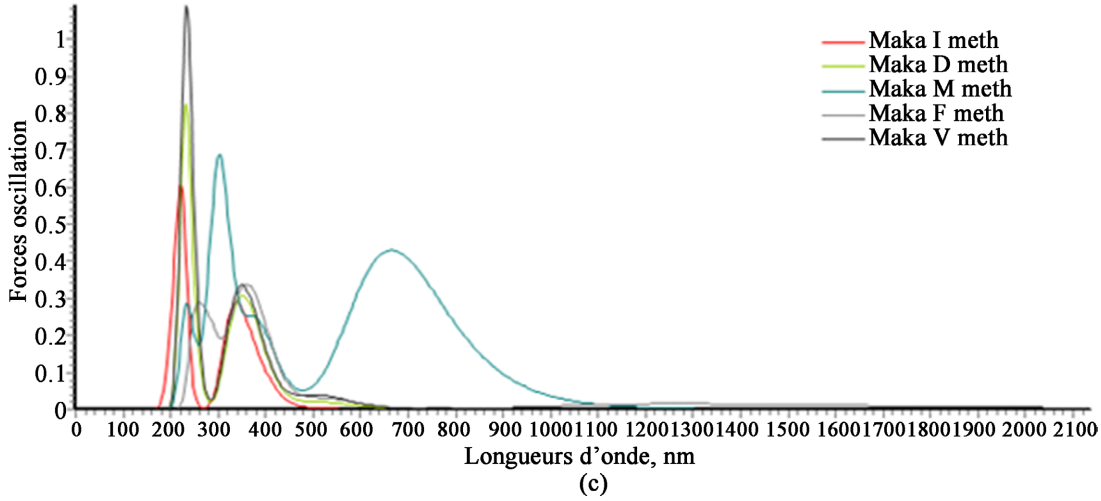


Figure 4. UV visible absorption spectra of Group 2 makaluvamines compared with the reference molecule. (a) Neutral makaluvamines; I, D, M, F and V; (b) Protonated makaluvamines; IH^+, DH^+, MH^+, FH^+ and VH^+; (c) Methylated makaluvamines; IMet, DMet, LMet, FMet and VMet.

molecules I, D, F, and V. Makaluvamine M absorbs from around 220 to 850 nm. This molecule absorbs over a wider range. However, each of these Makaluvamines absorbs in the ultraviolet as well as the visible. Compared to Makaluvamine I, the absorption bands of Makaluvamines D, F, and V each show a single peak with higher intensity. Each of these has a shoulder which is observed at the same wavelength as the second peak of Makaluvamine I. Makaluvamine M has two absorption maxima. The first is very intense and is observed at the same wavelength (around 330 nm) as the shoulders of Makaluvamines D, F, and V. The second is of low intensity at around 600 nm. **Figure 4(b)** and **Figure 4(c)** show the absorption bandwidths of protonated and methylated Group 2 and I Makaluvamines, respectively. It appears that for these charged molecules, absorption peak intensities have increased compared to neutral forms. Makaluvamine M is an exception. The absorption bands of MH^+ and MMet extend over a range from 200 to 1020 nm. These structures absorb both the ultraviolet and visible wavelengths. The intensities of the two absorption maxima of the MH^+ and MMet structures are modified. The first decreases in intensity, and the second increases. Overall, the absorption peak intensities of group 2 Makaluvamines are all modified when they are either protonated or methylated. The majority are stronger.

For Makaluvamine I and those of group 2, the principal electronic transitions among those generated with TD-DFT calculations, the wavelength values of the absorption maxima, the energy gaps between the transition levels, and the lifetime (τ) of the transition [18] are grouped together in **Table 2**.

The wavelength values of the absorption maxima (λ_{max})of these neutral, protonated and methylated Makaluvamines range from 220.8 nm to 668.2 nm. These maxima are observed in the ultraviolet. When Makaluvamines L and M are protonated or methylated, the maximum absorption, hence wavelength λ_{max} is observed in the visible. Both structures, therefore, absorb in the therapeutic domain

Table 2. Energy gap (eV), maximum wavelength (nm), lifetimes of principal transitions (ns) for Makaluvamines I and Group 2.

Molecules	ΔE	λ_{max}	τ	Principal Transition
I	3.22	238.7	33.03	HOMO → $LUMO_{+2}$ (89%)
D/J	3.06	250.8	26.08	HOMO → $LUMO_{+4}$ (53%)
F	2.86	331.9	57.67	$HOMO_{-3}$ → LUMO (93%)
M/L	2.42	335.0	28.00	HOMO → $LUMO_{+1}$ (93%)
V	3.10	248.0	22.13	HOMO → $LUMO_{+4}$ (89%)
IH^+	3.11	220.8	12.74	HOMO → $LUMO_{+1}$ (91%)
DH^+/JH^+	2.06	230.7	11.29	$HOMO_{-1}$ → $LUMO_{+1}$ (76%)
FH^+	1.32	250.6	45.01	HOMO → $LUMO_{+8}$ (64%)
MH^+/LH^+	1.97	668.2	155.80	HOMO → LUMO (100%)
VH^+	1.94	233.7	16.31	HOMO → $LUMO_{+4}$ (74%)
IMet	3.11	222.5	14.19	HOMO → $LUMO_{+1}$ (87%)
DMet/JMet	1.73	230.0	11.61	$HOMO_{-2}$ → $LUMO_{+1}$ (77%)
FMet	1.40	382.5	127.98	$HOMO_{-4}$ → $LUMO_{+1}$ (97%)
MMet/LMet	1.99	665.7	155.02	HOMO → LUMO (100%)
VMet	2.02	232.5	13.07	$HOMO_{-2}$ → $LUMO_{+1}$ (54%)

[7]. They, therefore, satisfy the condition for the spectral absorption of a photosensitizer. What's more, in these structures (LH+/MH+ and LMet/MMet), the principal electronic transitions occur only between the HOMO and the LUMO. They are of the n → π* type. These transitions have much longer lifetimes, estimated at around 155 ns. In addition, their energy gaps are small. This indicates a high reactivity of these molecular ions. All these results would proceed in favor of these forms of Makaluvamines for their photosensitizing properties. For the other Makaluvamines in group 2, transitions take place either between HOMO and a $LUMO_{+n}$ (n = 1 or 2 or 4 or 8), or between a HOMO-n (n = 1 or 2 or 3 or 4) and LUMO or $LUMO_{+1}$. These different transitions have shorter lifetimes, ranging from 11.29 ns to 127.98 ns. All these transitions are of the π → π* type [19]-[21].

3.3. Comparison of Spectroscopic Parameters of Group 3 Makaluvamines and the Reference

The UV-visible absorption spectra of Makaluvamines I, E/G and K/P (a); IH^+, EH^+/GH^+ and KH^+/PH^+ (b) and IMet, EMet/GMet and KMet/PMet (c) are shown in **Figure 5**.

As with reference to Makaluvamine I, the absorption band of Makaluvamine K/P extends from 180 nm to 600 nm (**Figure 5(a)**). Makaluvamine E/G absorbs from around 220 to 850 nm. The absorption bands of the reference molecule and Makaluvamine K/P have two maxima with slightly different intensities. Makaluvamine

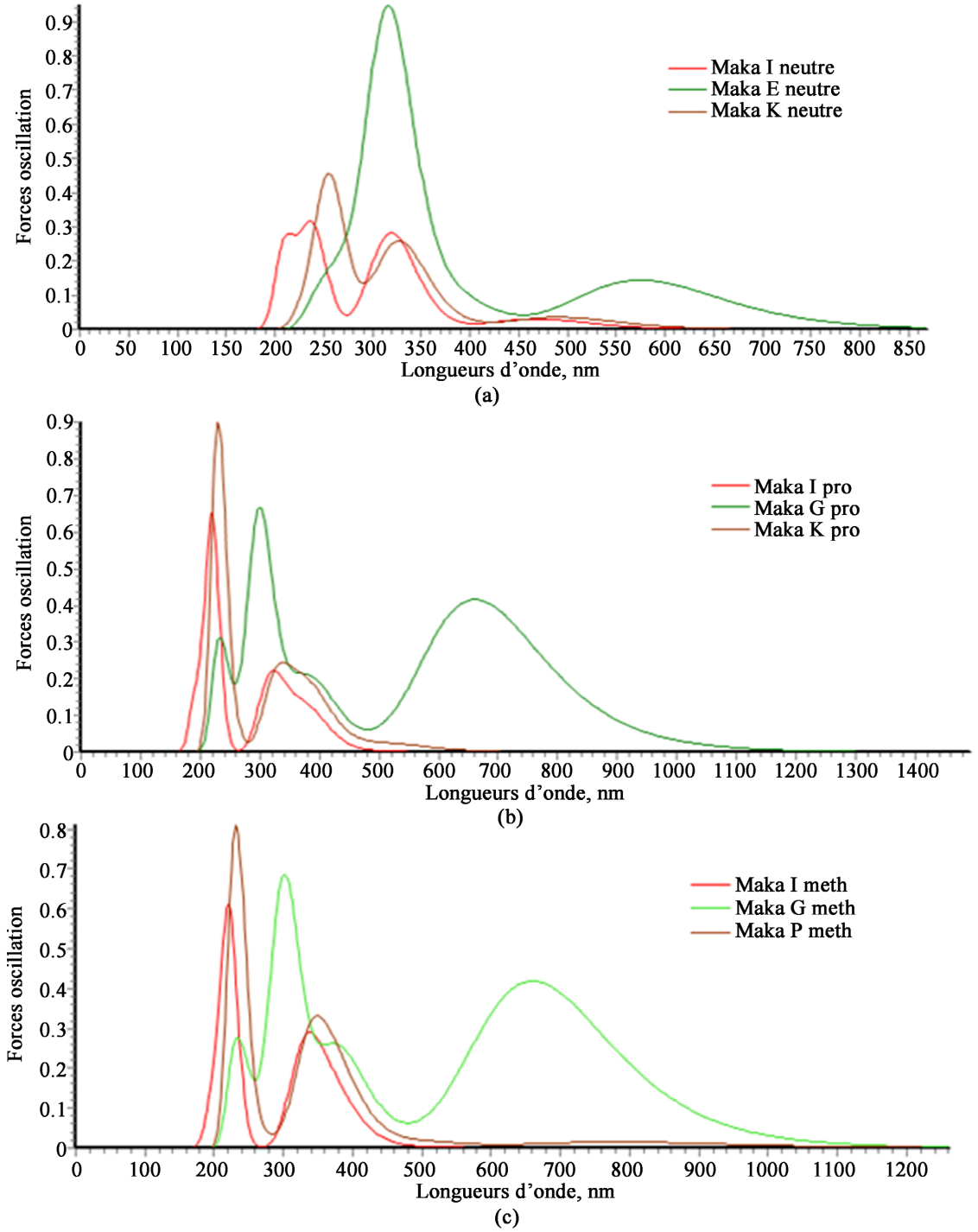


Figure 5. UV visible absorption spectra of Group 3 makaluvamines compared with the reference molecule. (a) Neutral makaluvamines; I, E/G and K/P; (b) Protonated makaluvamines; IH^+, EH^+/GH^+ and KH^+/PH^+; (c) Methylated makaluvamines; IMet, EMet/GMet and KMet/PMet.

E/G has one very intense peak and a second of low intensity.

Figure 5(b) and Figure 5(c) show that the absorption band extents of these protonated or methylated Makaluvamines are slightly modified. The intensities of the absorption peaks are also shown to be modified compared with those of the

neutral forms. Makaluvamines E/G are the exception to these findings. The absorption bands of EH^+/GH^+ and EMet /GMet range from 200 to 1100 nm. These structures absorb both the ultraviolet and visible wavelengths. The intensities of the two absorption maxima of EH^+/GH^+ and EMet /GMet are modified. The first peak decreases in intensity while the second increases.

In the end, the absorption intensities of group 3 Makaluvamines are all modified when they are either protonated or methylated. They are very often stronger.

For all these molecules, the principal electronic transitions among those generated with TD-DFT calculations, the wavelength values of the absorption maxima, the energy gaps between the transition levels, and the lifetime (τ) of the transition [18] are grouped together in Table 3.

Table 3. Energy gap (eV), maximum wavelength (nm), lifetimes of principal transitions (ns) for Makaluvamines I and group 3.

Molecules	ΔE	λ_{max}	τ	Principal Transition
I	3.22	238.7	33.03	HOMO → $LUMO_{+2}$ (89%)
E/G	2.56	319.1	22.62	HOMO → $LUMO_{+1}$ (83%)
K/P	3.07	323.2	74.08	$HOMO_{-2}$ → LUMO (87%)
IH^+	3.11	220.8	12.74	HOMO → $LUMO_{+1}$ (91%)
EH^+/GH^+	1.98	632.7	93.07	HOMO → LUMO (100%)
KH^+ (PH^+)	1.75	228.6	10.36	$HOMO_{-2}$ → $LUMO_{+1}$ (75%)
IMet	3.11	222.5	14.19	HOMO → $LUMO_{+1}$ (87%)
EMet/GMet	2.03	660.6	156.81	HOMO → LUMO (100%)
KMet/PMet	2.04	230.5	21.24	$HOMO_{-2}$ → $LUMO_{+1}$ (52%)

The wavelengths λ_{max} of the absorption maxima of all these Makaluvamines (neutral, protonated, and methylated) range from 220.8 nm to 660.6 nm. These are observed in the ultraviolet, but in the visible only for Makaluvamines EH^+/GH^+ and EMet/GMet. These structures absorb in the therapeutic range (620 to 800 nm). They meet the absorption requirement for a substance that can act as a photosensitizer in photodynamic therapy. Consequently, their principal electronic transitions take place exclusively between the HOMO and LUMO frontier orbitals. These transitions are of the n → π* type. Their lifetimes are 93.07 ns and 156.81 ns, respectively. They are significantly longer than those of the other structures.

For the other Makaluvamines in group 3, transitions are mainly either between HOMO and $LUMO_{+n}$ (n = 1 or 2), or between $HOMO_{-2}$ and LUMO or $LUMO_{+1}$. These transitions have shorter lifetimes, ranging from 10.36 ns to 74.08 ns. All these transitions are of the π → π* type [19] [20] [21].

3.4. Comparison of Spectroscopic Parameters of Group 4 Makaluvamines and the Reference

Two Makaluvamines, N and O, form this group. Figure 6 below shows the UV

visible absorption spectra of Makaluvamines I, N and O (a); IH^+, NH^+ and OH^+ (b) then IMet, NMet, and OMet (c).

The UV visible absorption bands range from 180 to 600 nm for the three neutral Makaluvamines I, N, and O (Figure 6(a)). Each molecule exhibits two ultraviolet

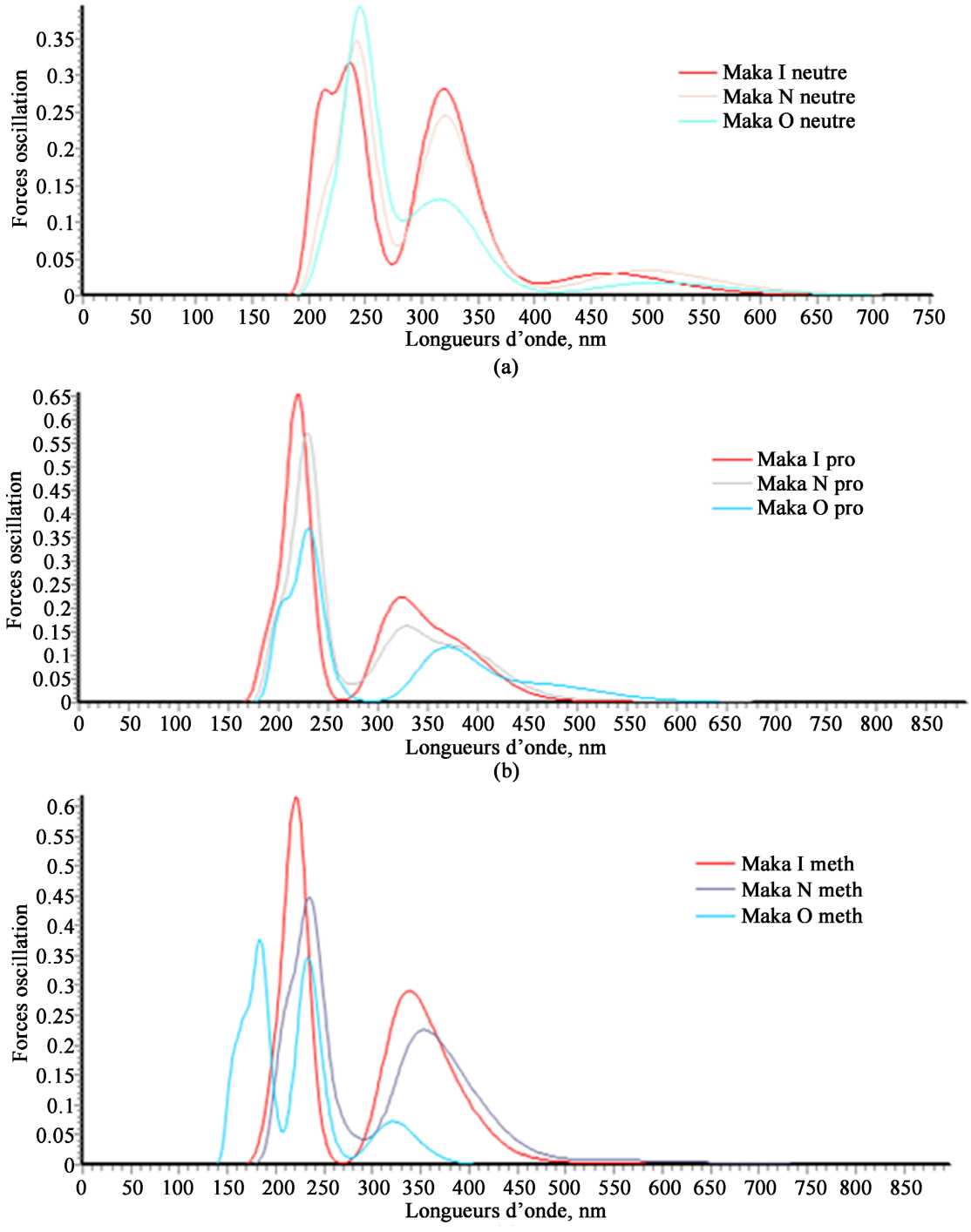


Figure 6. UV visible absorption spectra of Group 4 makaluvamines compared with the reference molecule. (a) Neutral makaluvamines; I, N and O; (b) Protonated makaluvamines; IH^+, NH^+ and OH^+; (c) Methylated makaluvamines; IMet, NMet, and Omet.

absorption peaks. For a given absorption peak, the λ_{max} values are virtually the same for all three molecules. The two absorption peaks of Makaluvamine I have similar intensities. Makaluvamine O's first peak is more intense than those of the other Makaluvamines, and its second is less intense.

Figure 6(b) and Figure 6(c) show the absorption spectra of the protonated and methylated forms, respectively. Compared with those in Figure 6(a), they show some modifications. In particular, the absorption band of Makaluvamine O. For Makaluvamines I and N, absorption peak intensities have increased. The methylation of O reveals three absorption maxima. The absorption region of O is also reduced between 140 nm and 390 nm.

For all these structures, the main electronic transitions among those generated with TD-DFT calculations, the wavelength values of the absorption maxima, the energy gaps between the transition levels, and the lifetime (τ) of the transition [18] are grouped together in Table 4.

Table 4. Energy gap (eV), maximum wavelength (nm), lifetimes of principal transitions (ns) for Makaluvamines I and Group 4.

Molecules	ΔE	λ_{max}	τ	Principal Transition
I	3.22	238.7	33.03	HOMO → $LUMO_{+2}$ (89%)
N	3.08	242.8	29.11	HOMO → $LUMO_{+2}$ (90%)
O	3.07	238.7	32.29	HOMO → $LUMO_{+1}$ (99%)
IH^+	3.11	220.8	12.74	HOMO → $LUMO_{+1}$ (91%)
NH^+	2.92	230.5	15.39	HOMO → $LUMO_{+1}$ (87%)
OH^+	3.24	231.3	29.77	HOMO → $LUMO_{+2}$ (75%)
IMet	3.11	222.5	14.19	HOMO → $LUMO_{+1}$ (87%)
NMet	2.85	237.1	21.76	HOMO → $LUMO_{+1}$ (84%)
OMet	9.16	232.8	23.46	$HOMO_{-1}$ → LUMO (90%)

The wavelengths λ_{max} of the absorption maxima of these Makaluvamines (neutral, protonated, and methylated) are all observed in the ultraviolet. They range from 220.8 nm to 242.8 nm. The principal electronic transitions associated with these absorptions are between HOMO and either $LUMO_{+1}$ or $LUMO_{+2}$. One exception is observed in OMet. The transition involves $HOMO_{-1}$ and LUMO. All the transitions observed are of the $\pi \rightarrow \pi^*$ type [19]-[21]. Their lifetimes are short, ranging from 12.74 ns to 33.03 ns. The energy gaps in these structures are relatively large compared with those in the others. That of Makaluvamine OMet is very apparent. It reflects the great stability of this structure.

Finally, none of the structural forms of the Makaluvamines in Table 4 are absorbed in the therapeutic domain.

4. Conclusions

To carry out this study of the spectroscopic properties of the Makaluvamines

series listed in the literature, we performed "single point" calculations at the TD-DFT // B3LYP/6-311++G(d,p) level of theory. Gaussian 09 software was used for these calculations. A second software package, Chemissian, was used to access the spectroscopic data of the molecules. We determined:

- Absorption spectra in the visible ultra-violet range. These provide information on the absorption bandwidths of molecules.
- Wavelength values of absorption maxima.
- The main electronic transitions associated with absorption maxima and their lifetimes

With the exception of Makaluvamines M/L and E/G, the transition from the neutral to the charged (protonated or methylated) form induces a decrease in the wavelength of the absorption peak. The same applies to the lifetime of the associated transition. For Makaluvamines M/L and E/G, absorption peak wavelengths almost double when protonated or methylated. The HOMO and LUMO frontier orbitals are close together in these structures. In these charged molecules (protonated or methylated), the principal electronic transitions take place exclusively between the HOMO and LUMO frontier orbitals. Their lifetimes are very long compared with those of neutral forms. MH^+/LH^+, MMet/LMet, EH^+/GH^+, and EMet/GMet molecules absorb in the therapeutic range (620 nm to 800 nm). They also have longer lifetimes in their excited states. They could possess photosensitizer properties for use in photodynamic cancer therapy.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

[1] Asrani, S.K., Devarbhavi, H., Eaton, J. and Kamath, P.S. (2019) Burden of Liver Diseases in the World. *Journal of Hepatology*, **70**, 151-171. https://doi.org/10.1016/j.jhep.2018.09.014

[2] Raab, O. (1900) Uber die wirkung fluoreszierenden stoffen. *Infusaria Zeitschrift Biologie*, **39**, 524.

[3] Tappeiner, H.V. and Jesoniek, A. (1903) Therapeutische versuchi mit fluoreszeirender stoff. *Münchener Medizinische Wochenschrift*, **1**, 2042-2044.

[4] Dougherty, T.J., Kaufman, J.E. and Goldfarb, A. (1978) Photoirradiation Therapy for the Treatment of Malignant Tumors. *Cancer Research*, **38**, 2628-2635.

[5] Gunasekera, S.P., Zuleta, I.A., Longley, R.E., Wright, A.E. and Pomponi, S.A. (2003) Discorhabdins S, T, and U, New Cytotoxic Pyrroloiminoquinones from a Deep-Water Caribbean Sponge of the Genus Batzella. *Journal of Natural Products*, **66**, 1615-1617. https://doi.org/10.1021/np030292s

[6] Radisky, D.C., Radisky, E.S., Barrows, L.R., Copp, B.R., Kramer, R.A. and Ireland, C.M. (1993) Novel Cytotoxic Topoisomerase II Inhibiting Pyrroloiminoquinones from Fijian Sponges of the Genus Zyzzya. *Journal of the American Chemical Society*, **115**, 1632-1638. https://doi.org/10.1021/ja00058a003

[7] Muriel, B.-H., Céline, F., *et al.* (2007) La thérapie photodynamique. *L'actualité Chimique*, No. 308-309, 26.

[8] Seck, I., Sall, M.L., Ndiaye, A., Ndoye, S.F., Ba, L.A. and Seck, M. (2023) Spectroscopic Electrochemical Properties and DFT Calculation of 1-Aryltriazenes. *International Journal of Organic Chemistry*, **13**, 109-128. https://doi.org/10.4236/ijoc.2023.134009

[9] Matin, M.A., Bhattacharjee, S., Shaikh, M.A.A., Debnath, T. and Aziz, M.A. (2020) A Density Functional Theory (DFT) Investigation on the Structure and Spectroscopic Behavior of 2-Aminoterephthalic Acid and Its Sodium Salts. *Green and Sustainable Chemistry*, **10**, 39-55. https://doi.org/10.4236/gsc.2020.102004

[10] Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., *et al.* (2009) Gaussian 09, Revision A.02. Gaussian, Inc.

[11] Hohenberg, P. and Kohn, W. (1964) Inhomogeneous Electron Gas. *Physical Review*, **136**, B864-B871. https://doi.org/10.1103/physrev.136.b864

[12] Casida, M.E., Jamorski, C., Casida, K.C. and Salahub, D.R. (1998) Molecular Excitation Energies to High-Lying Bound States from Time-Dependent Density-Functional Response Theory: Characterization and Correction of the Time-Dependent Local Density Approximation Ionization Threshold. *The Journal of Chemical Physics*, **108**, 4439-4449. https://doi.org/10.1063/1.475855

[13] Tozer, D.J., Amos, R.D., Handy, N.C., Roos, B.O. and Serrano-Andres, L. (1999) Does Density Functional Theory Contribute to the Understanding of Excited States of Unsaturated Organic Compounds? *Molecular Physics*, **97**, 859-868. https://doi.org/10.1080/00268979909482888

[14] Gross, E.K.U., Dobson, J.F. and Petersillka, M. (1996) Density Functional Theory. Springer.

[15] Koch, W. and Holthausen, M.C. (1999) A Chemist's Guide to Density Functional Theory. 2nd Edition, Wiley-VCH.

[16] Casida, M.E. (1995) Time-Dependent Density Functional Response Theory for Molecules. In: *Recent Advances in Computational Chemistry*, World Scientific, 155-192. https://doi.org/10.1142/9789812830586_0005

[17] Li, M., Kou, L., Diao, L., Zhang, Q., Li, Z., Wu, Q., *et al.* (2015) Theoretical Study of Ws-9-Based Organic Sensitizers for Unusual Vis/Nir Absorption and Highly Efficient Dye-Sensitized Solar Cells. *The Journal of Physical Chemistry C*, **119**, 9782-9790. https://doi.org/10.1021/acs.jpcc.5b03667

[18] Lukeš, V., Aquino, A. and Lischka, H. (2005) Theoretical Study of Vibrational and Optical Spectra of Methylene-Bridged Oligofluorenes. *The Journal of Physical Chemistry A*, **109**, 10232-10238. https://doi.org/10.1021/jp054248s

[19] Laëtitia, D. (2007) Apport des spectroscopies moléculaires à l'étude des mécanismes de fixation des ions métalliques polluants sur les substances chimiques. Complexation de Al (III), Pb (II) et Zn (II) par des systèmes modèles. Université des Sciences et Technologie de Lille.

[20] Wachsman, E.D. and Frank, C.W. (1988) Effect of Cure History on the Morphology of Polyimide: Fluorescence Spectroscopy as a Method for Determining the Degree of Cure. *Polymer*, **29**, 1191-1197. https://doi.org/10.1016/0032-3861(88)90043-2

[21] Ranjan, S., Lin, S., Hwang, K., Chi, Y., Ching, W., Liu, C., *et al.* (2003) Realizing Green Phosphorescent Light-Emitting Materials from Rhenium (I) Pyrazolato Diimine Complexes. *Inorganic Chemistry*, **42**, 1248-1255. https://doi.org/10.1021/ic0259181

[22] Hachi, M.S., El Khattabil, A., Fitril, A., *et al.* (2018) DFT and TD-DFT Studies of the π-Bridge Influence on the Photovoltaic Properties of Dyes Based on Thieno[2, 3-b]indole. *Journal of Materials and Environmental Science*, **9**, 1200-1210.