

สมบัติเคมีเชิงแสงและกายภาพเชิงแสงของอนุพันธ์ซินนามต



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**PHOTOCHEMICAL AND PHOTOPHYSICAL PROPERTIES OF CINNAMATE
DERIVATIVES**

Miss Thitinun Monhaphol

**A Dissertation Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy Program in Chemistry**

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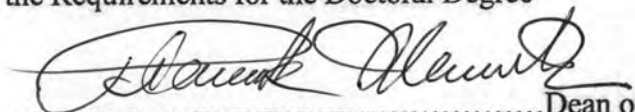
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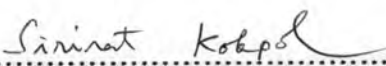
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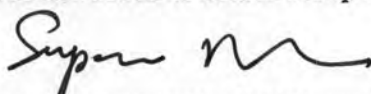
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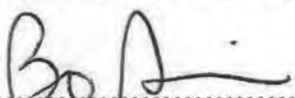
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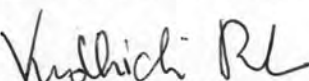

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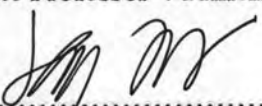
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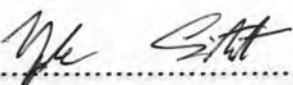

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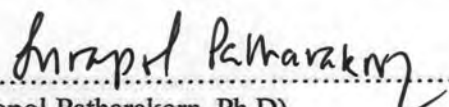

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งานวิจัยนี้เป็นการสังเคราะห์ซินนามตที่มีหมู่แทนที่เป็นเมทอกซีที่ตำแหน่งต่างกันบนวงฟีนิลลิบชนิด และศึกษาสมบัติเคมีเชิงแสงของสารทั้งลิบ นอกจากนี้ได้ศึกษาสมบัติทางกายภาพเชิงแสงของ 2-เอทิลเฮกซิลซินนามต หัวขนิคจากลิบชนิดดังกล่าว โดยศึกษาจากการทดลองและจากการคำนวณพบว่า การเปล่งแสงฟลูออเรสเซน เปลี่ยนแปลงอย่างชัดเจนตามตำแหน่งการแทนที่ของหมู่เมทอกซีบนวงฟีนิล ซินนามตที่มีหมู่เมทอกซีที่ตำแหน่งเมตาเกิดการเปล่งแสงอย่างชัดเจน ขณะที่ซินนามตที่มีหมู่แทนที่พาราเกิดการเปล่งแสงน้อยมาก ลักษณะดังกล่าวนี้สอดคล้องกับการเปลี่ยนแปลงรูปแบบของสเปกตรัมการดูดกลืนรังสียูวี กล่าวคือระดับพลังงานของสภาวะกระตุ้นแบบพาย-พายที่มีพลังงานต่ำสุดสองระดับของซินนามตที่มีหมู่เมทอกซีที่ตำแหน่งเมตามีพลังงานต่างกันมาก ขณะที่ระดับพลังงานทั้งสองของซินนามตที่มีหมู่แทนที่ที่ตำแหน่งพาราต่างกันน้อยมากหรือไม่แยกออกจากกัน ซึ่งสอดคล้องกับค่าระดับพลังงานกระตุ้นที่ทำให้พันธะคู่บิดไปและกลับสู่สภาวะพื้นแบบไม่เปล่งแสง ด้วยการคำนวณควอนตัม โดยวิธี เชมิ เอ็มไพริคัล และด้วยการทดลอง พบว่า ซินนามตที่มีหมู่เมทอกซีที่ตำแหน่งเมตา ต้องใช้พลังงานนี้มากกว่าซินนามตที่มีหมู่แทนที่ที่ตำแหน่งพารา ดังนั้นจึงบ่งได้ว่าซินนามตที่มีหมู่เมทอกซีที่ตำแหน่งพารากลับสู่สภาวะพื้น แบบไม่เปล่งแสง และซินนามตที่มีหมู่แทนที่ที่ตำแหน่งเมตา กลับสู่สภาวะพื้นเป็นแบบเปล่งแสง ซึ่งจากผลของหมู่แทนที่ที่ตำแหน่งเมตานิ ทำให้ซินนามตที่มีหมู่แทนที่ที่ตำแหน่ง 2 4 และ 5 บน วงฟีนิลที่มีการเปล่งแสงมากกว่า ซินนามตที่มีหมู่แทนที่ที่ตำแหน่ง 2 4 และ 6

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The syntheses and photochemical properties of ten methoxy substituted cinnamates were carried out and the photophysical properties of five selected methoxy substituted 2-ethylhexyl-cinnamates were studied. Both experimental and theoretical methods indicated that the fluorescence quantum yields varied strongly with the substituted position on the phenyl ring. A methoxy substitution at meta position gave strong fluorescence whereas the para substituted compounds were strongly quenched. This observation could be correlated to the corresponding changes in the UV absorption spectra; the two lowest $\pi\pi^*$ states were split for the meta-substituted cinnamates but almost degenerate for the para compounds. Semi-empirical quantum calculation confirmed the observed state ordering and supported the difference in the experimentally determined activation energies for non-radiative decay. This "meta-effect" could be applied for the trimethoxy substituted compounds: strong fluorescence with relatively high barrier for non-radiative decay in 2,4,5- and weak fluorescence with relatively low barrier for non-radiative decay in 2,4,6-trimethoxycinnamate.

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List of Abbreviations

a_0	radius of solvent cavity
br	broad
c	speed of light (2.80×10^8 m / s; equation 2.5)
$^{\circ}\text{C}$	degree Celsius
cm^{-1}	unit of wavenumber (IR)
cm^{-1}	per centimeter (s)
Cpd	compound
d	doublet (NMR)
exp	exponential
FGH	frequency harmonic generator (TCSPC)
ϕ_f	Fluorescence quantum yield
g	gram (s)
h	Plank's constant (equation 2.5)
Hz	hertz
ΔH_f	heat of formation
IC	internal conversion
IR	infrared
ISC	intersystem crossing
J	coupling constant
kcal	kilo calori
k_f	radiative rate constant
k_{nr}	non-radiative rate constant
lit	literature
m	multiplet (NMR)
min	minute (s)
mL	milliliter (s)
mmol	millimole
m.p.	melting point
MS	mass spectrometry

m/z	mass per charge
μ_g, μ_e	ground state and excited state
n	refractive index (equation 2.6)
nm	nanometer (s)
NMR	nuclear magnetic resonance
ns	nanosecond
$\tilde{\nu}$	wavenumber
ppm	parts per million
ps	picosecond
q	quartet (NMR)
s	singlet (NMR)
t	triplet (NMR)
TCSPC	Time-correlated single photon counting
τ_f	fluorescence lifetime
$\langle \tau \rangle_f$	average fluorescence lifetime
δ	chemical shift
%	percent
λ	wavelength
ϵ	molar absorptivity
ϵ	solvent dielectric constant (equation 2.6)
UV	ultraviolet
W	watt (light intensity unit)
X^2	chi square