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ANION AND AMINO ACID SENSORS AND LUMINESCENCE MOLECULAR LOGIC GATES

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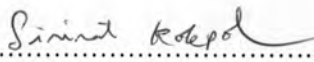
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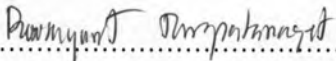
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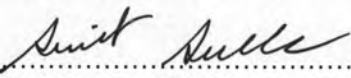
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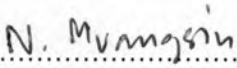
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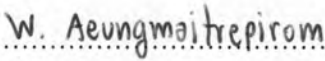
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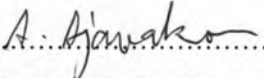
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ได้ทำการสังเคราะห์ L^1H และ L^2H สำหรับเป็นเซนเซอร์ใหม่ที่ใช้การเปลี่ยนแปลงสีจากอนุพันธ์ของเบนซิมิดาโซล และแอนทราควิโนน ในสภาวะที่มีไอออนของฟลูออไรด์ อะซิเตด ไดไฮโดรเจนฟอสเฟต ที่พันธะ $-NH_{car}CH_2N_{imi}^-$ ของ L^1H จะแตก และ โปรตอนตำแหน่งเอไมด์ทั้งสองจะหลุดออกมีผลทำให้โมเลกุล L^1H เปลี่ยนเป็น L^3H ส่วน L^2H จะเกิดการหลุดของโปรตอนที่ตำแหน่งเอไมด์ของหน่วยแอนทราควิโนน ทำให้เกิดปรากฏการณ์การเปลี่ยนสีเนื่องจากเกิดการส่งผ่านประจุ การศึกษาสมบัติทางเคมีไฟฟ้าพบว่า L^2H ตอบสนองต่อฟลูออไรด์ เพราะพีครีดักชันจะมีการเปลี่ยนแปลงไปที่ศักย์ไฟฟ้าที่มีค่าลบมากขึ้น L^2H สามารถแยกแอนไอออนเป็นสามกลุ่มขึ้นกับความเข้มข้นของแอนไอออน ส่วนกรดอะมิโน (ทริปโตฟาน ฟีนิลอะลานีน และ อะลานีน) สามารถเกิดพันธะกับไดแอนไอออน โดยใช้พันธะไฮโดรเจน และแรงระหว่างประจุ และที่น่าสนใจคือ กรณี L^3H ในรูป รีดิทซ์จะพบว่ามีความเลือกจำเพาะในการจับกับไดไฮโดรเจนฟอสเฟตได้ดีมาก นอกจากนี้ L^3H ยังบอกความแตกต่างของ อีแนนทิโอเมอร์ของฟีนิลอะลานีน ในรูป L- และ D- ได้ ส่วน Trp นั้น L^3H ไม่สามารถจำแนกอีแนนทิโอเมอร์ได้ในรูปแบบ D- และ L- จากการสังเกตพีคที่เหมือนกัน

ได้ทำการเตรียมโมเลกุลทางตรรกศาสตร์ภายในโมเซลล์โดยผ่านการเกิดเซลล์ไฟ-แอสเซมบลีของฟลูออฟอร์ (23, 24, 25 และ 26) และรีเซปเตอร์ (8b, 10b, 27, 28, 29, 30 และ 31) ผลการทดลองแสดงพฤติกรรม "ปลั๊กและเพล" จากการเลือกองค์ประกอบของรีเซปเตอร์ ฟลูออโรฟอร์ และโมเซลล์ อย่างละ 1 ชนิดหรือมากกว่านั้นขึ้นอยู่กับการนำไปใช้งาน ระบบ "ปลั๊กและเพล" ได้ประสบความสำเร็จในทางตรรกศาสตร์ เช่น พาส ศูนย์, พาส หนึ่ง, ใช่, ไม่ใช่, หรือ และ และนอกจากนี้ได้ทำการสังเคราะห์โพลไซลีน (12b, 13b, 15b, 16b, 18b และ 20b) สำหรับเป็นฟลูออเรสเซนต์เซนเซอร์ ที่มีการตอบสนองต่อโปรตอนบนพื้นผิวของเม็ดบีด โพลไซลีนบางชนิดแสดงพฤติกรรมในสารละลายเนื้อเดียวกันเป็นโมเลกุลทางตรรกศาสตร์ชนิดรีคอนฟิเกอเรชัน การถ่ายโอนประจุภายในโมเลกุลของสภาวะกระตุ้นโพลไซลีนนั้นยืนยันโดยการเปลี่ยนแปลงของความยาวคลื่นที่เพิ่มขึ้นของช่วงการคายพลังงานซึ่งเป็นไปตามความมีขั้วมากของตัวทำละลาย

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BOONTANA WANNALERSE: ANION AND AMINO ACID SENSORS AND LUMINESCENCE LOGIC

GATES. THESIS ADVISOR: ASSOC. PROF. THAWATCHAI TUNTULANI, Ph.D.,

THESIS COADVISOR: ASST. PROF. BOOSAYARAT TOMAPATANAGET, Ph.D, 160 pp.

Novel colorimetric sensors, L^1H and L^2H , derived from imidazolium and anthraquinone moieties were synthesized. In the presence of F^- , AcO^- and $H_2PO_4^-$, $-NH_{car}-CH_2-N_{imi}-$ of L^1H was cleaved and both amide protons were deprotonated. L^1H structure is changed to be L^3H form. L^2H was found to undergo deprotonation processes of the $NH-$ moiety of the amide-anthraquinone unit. These phenomena gave a dramatic color change due to charge transfer transition. Electrochemical studies showed that L^2H responded to F^- because the electrochemical reduction peaks were shifted to more negative potential. L^2H is able to discriminate the three group of anion depending on the basicity of anions. Moreover, amino acids (Trp, Phe and Ala) were able to bind dianion using hydrogen bonding and electrostatic force. Interestingly, the reduced form of L^3H has excellent selectivity to $H_2PO_4^-$. Moreover, L^3H can differentiate the enantioselectivity of Phe but it is not able to discriminate the enantiomer of Trp, namely D- and L- forms observing from the analogous peaks.

Molecular logic gates in micelles were successfully demonstrated using self-assembly of fluorophores (23, 24, 25 and 26) and receptors (8b, 10b, 27, 28, 29, 30 and 31) within a detergent micelle compartment. Moreover, the results show 'plug and play' behaviour since a given combination of one or more receptors, fluorophore and micelle could be selected as the system for a particular use. The 'plug and play' was shown with various types of logic gates such as PASS 0, PASS 1, YES, NOT, OR and AND were achieved. Additionally, new pyrazolines (12b, 13b, 15b, 16b, 18b and 20b) were synthesized for use as fluorescent sensors and switches responding to protons for eventually use on bead surfaces. Some of these pyrazolines behave in homogeneous solution as reconfigurable molecular logic gates. The internal charge transfer (ICT) nature of pyrazoline excited states was confirmed by the red shift of the emission wavelength as the polarity of the solvent is increased.

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LIST OF ABBREVAITIONS

Å	Angstrom
K_{ass}	Association constant
$^{13}\text{C-NMR}$	Carbon Nuclear Magnetic Resonance
°C	Degree Celcius
δ	Chemical shift
J	Coupling constant
g	Gram
Hz	Hertz
MALDI-TOF	Marrix Assistance Laser Desorptioin/Ionization-Time of Flight
mL	Milliliter
mmol	Millimol
ppm	Part per million
M^{-1}	Per molar
$^1\text{H-NMR}$	Proton Nuclear Magnetic Resonance
RT	Room temperature
CV	Cyclic Voltammetry
SW	Square Wave Voltammetry
A	Ampere
V	Volt
E	Potential
F	Faraday constant
TBAFP	Tetrabutylammonium hexafluorophosphate
DMSO	Dimethyl sulfoxide
Bu_4N	Tetrabutylammonium
ESI-TOF MS	Electronspray Ionization Time of Flight Mass Spectrometry
AQ	Anthraquinone
AQ^-	Semiquinone
AQ^{2-}	Dianion
AcO^-	Acetate
BzO^-	Benzoate
Ala	Alanine

Trp	Tryptophan
Phe	Phenyl alanine
equiv.	Equivalents
FE	Fluorescence Enhancement