

**SUPRAMOLECULAR STRUCTURES AND MOLECULAR SELF-
ASSEMBLY UNDER HYDROGEN BONDED AND/ OR METAL
COORDINATED CASE STUDIES: FROM BENZOXAZINES TO
DIACETYLENE**

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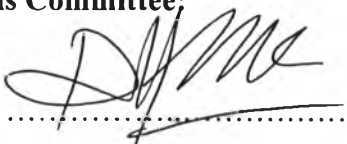
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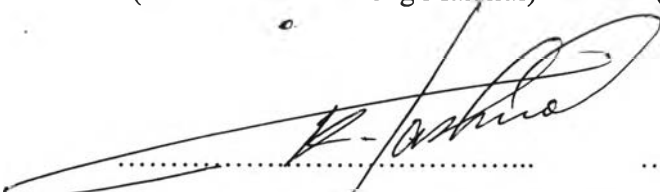
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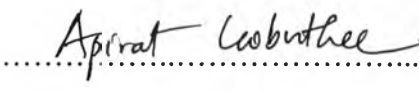

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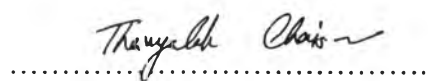

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ABSTRACT

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The present work focuses on molecular design and development of molecular self-assembly via hydrogen bond network and/ or metal coordination through the case studies on benzoxazines and diacetylenes. In the first part shows the unique molecular design of benzoxazines by using diamines so that the ring opening structured diamine-based benzoxazine dimers favour the continuous hydrogen bond network and metal complexation. By simply varying hydrophobic (methylene) bridge length and concentration, the self-assembly of diamine-based benzoxazine under hydrogen bond network can be clarified and also performed the various morphologies. Not only formation of hydrogen bonding but also coordination with metal ion, the diamine-based benzoxazines are proved to be supramolecular polymer via both hydrogen bonding and metal-ligand complexation which have been rarely seen. From this study, the diamine-based benzoxazine dimer can be noticed to be one of the choices for modifying terminated moiety of macromonomer in order that chain growth can be able to form supramolecular polymers. In the final part, the work covers supramolecular structures of diacetylene derivatives (diarylbutadiyne) which topochemical polymerization can be carried out. In fact, the successful cases of diarylbutadiyne solid state polymerization are few reported. This work shows the effect of substituted positions (ortho-, meta-, and para positions) of conjugated amide

under photon irradiation. Hydrogen bond network of amide unit is used for preforming structures to reach the optimum packing, favouring the topochemical polymerization. The solid state polymerization of *N,N'*-(3,3'-(buta-1,3-diyne-1,4-diyl)bis(3,1-phenylene))diheptanamide (mDA) is faster than the others, whereas *N,N'*-(4,4'-(buta-1,3-diyne-1,4-diyl)bis(4,1-phenylene))diheptanamide (pDA) is not polymerized under the light. The total change in volume of polymer and monomer crystals is clarified to explain the possibility of their topochemical polymerization.

บทคัดย่อ

พิมพ์สาข ดันภินาต : กรณีศึกษาโครงสร้างซูปราโมเลกุลและการจัดเรียงตัวเองในระดับโมเลกุลภายใต้พันธะไฮโดรเจน และ/ หรือ โลหะโคออร์ดิเนชัน: จากเบนซอกซาซีนสู่ไดอะเซทิลีน (Supramolecular Structures and Molecular Self-assembly under Hydrogen Bonded and/ or Metal Coordinated Case Studies: From Benzoxazines to Diacetylenes) อ. ที่ปรึกษา: ศาสตราจารย์ ดร. สุวบุญ จิราญชัย 100 หน้า

วิทยานิพนธ์ฉบับนี้มุ่งเน้นไปที่การออกแบบและพัฒนาการจัดเรียงตัวเองในระดับโมเลกุลผ่านพันธะไฮโดรเจน และ/หรือ โลหะโคออร์ดิเนชันจากกรณีศึกษาของเบนซอกซาซีนและไดอะเซทิลีน โดยในครั้งแรกเป็นการแสดงถึงการออกแบบโมเลกุลเบนซอกซาซีนที่มีลักษณะเฉพาะ โดยการใช้ไดเอมีน ทำให้ได้โครงสร้างจากการเปิดวงเป็นเบนซอกซาซีนไดเมอร์ซึ่งสนับสนุนการเกิดโครงข่ายพันธะไฮโดรเจนและโลหะโคออร์ดิเนชันที่ต่อเนื่อง การปรับเปลี่ยนความยาวของหมู่ไฮโดร โฟบิก (เมทิลีน) และความเข้มข้นของสารละลายเบนซอกซาซีนไดเมอร์ทำให้สามารถบ่งชี้รายละเอียดของการจัดเรียงตัวเองในระดับ โมเลกุลของเบนซอกซาซีนไดเมอร์ภายใต้โครงข่ายพันธะไฮโดรเจนได้ รวมทั้งทำให้ได้สัญญาณของการจัดเรียงตัวเองที่หลากหลาย นอกจากนี้เบนซอกซาซีนไดเมอร์ได้รับการพิสูจน์ทราบถึงการเกิดซูปราโมเลกุลาร์พอลิเมอร์ผ่านพันธะไฮโดรเจนและโคออร์ดิเนชันกับไอออนของโลหะ ซึ่งที่ผ่านมาไม่ค่อยมีการรายงานในประเด็นดังกล่าว จากการศึกษาทำให้สามารถกล่าวได้ว่าเบนซอกซาซีนไดเมอร์เป็นหนึ่งในตัวเลือกที่สามารถนำไปปรับเปลี่ยนโครงสร้างบริเวณหมู่ปลายของแมโครมอนอเมอร์ซึ่งเอื้อต่อการพัฒนาไปเป็นซูปราโมเลกุลาร์พอลิเมอร์ ในที่สุดทำผลงานวิจัยครอบคลุมถึงโครงสร้างซูปราโมเลกุลของอนุพันธ์ไดอะเซทิลีน (ไดเอริลบิวตะไดอายน) ที่สามารถเกิดทอพอเคมีคอล พอลิเมอร์เชชันได้ โดยที่ผ่านมาได้มีการรายงานเกี่ยวกับการพอลิเมอร์เชชันของอนุพันธ์ไดเอริลบิวตะไดอายนในสภาวะของแข็งค่อนข้างจำกัด งานวิจัยนี้แสดงให้เห็นถึงผลของหมู่แทนที่ตำแหน่งต่างๆ (ตำแหน่งออร์โท, เมทา และพารา) ของคอนจูเกตเอไมด์ต่อการพอลิเมอร์เชชันภายใต้การฉายรังสีโฟตอน โครงข่ายพันธะไฮโดรเจนของเอไมด์ถูกใช้เพื่อการสร้างโครงสร้างเริ่มแรก ให้เอื้อต่อการจัดเรียงตัวที่เหมาะสมในการเกิดโทโพเคมีคอล พอลิเมอร์เชชัน ซึ่งพบว่าการเกิดพอลิเมอร์เชชัน ใน ส ก ว ะ ข อ ง แ อ ง ข อ ง N,N' -(3,3'-(buta-1,3-diyne-1,4-diyl)bis(3,1-phenylene))diheptanamide (mDA) เร็วที่สุด ในขณะที่ N,N' -(4,4'-(buta-1,3-diyne-1,4-diyl)bis(4,1-phenylene))diheptanamide (pDA) ไม่สามารถเกิดพอลิเมอร์เชชันด้วยแสงได้

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