SYNTHESIS AND CHARACTERIZATION OF DISUBSTITUTED CONJUGATED ETHYNYLATED-IMINE DERIVATIVES AS POTENTIAL LIQUID CRYSTALLINE MATERIALS

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DEDICATION

My humble effort I dedicate to my eternal love;
Ayah, Ibu, Along and Baby

Whose affection, love, encouragement and prays of day and night make me able to get such success and honor.

"If you want the things you never had, you gotta do the things you've never done."
(Gary Vaynerchuk)

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Faculty : **Faculty of Science and Marine Environment**

A typical liquid crystalline material usually consists of rigid center, linker/bridge and flexible chain tail. By taking this in consideration, 15 novel compounds bearing ethynyl (C≡C), imine (C=N) and alkoxy chain were introduced through condensation process of primary amines and aldehydes. This highly conjugated molecules with general formula of Donor-Ar(C=N)Ar(C≡C)Ar(C=N)Ar-Donor are believed to exhibit liquid crystalline nature. All synthesized compounds were characterized spectroscopically and analytically via CHN Elemental Microanalysis, Fourier Transform Infrared (FTIR), Ultraviolet-Visible spectroscopy (UV-Vis), ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR), Thermogravimetric analysis (TGA), Scanning Electron Microscopy (SEM) and Cyclic voltammetry (CV) analysis. For liquid crystal study, Differential Scanning Calorimetry (DSC) and Polarized Optical Microscopy (POM) were carried out to give better understanding. The infrared spectra revealed the most significant bands of interest C=N and C≡C at 1617 – 1621 cm^{-1} and 2201 – 2209 cm^{-1} respectively which then were confirmed by the presence of C=N resonance around δ_H 8.31 – 8.39 ppm and δ_C 159.00 – 161.75 ppm in ^{1}H and ^{13}C NMR spectroscopies respectively. The π–π^* electronic transitions recorded in UV-Vis spectroscopy are believed to arise from the functional groups C=C (phenyl) and C≡C while C=N and OC_nH_{2n+1} resulted in the mixture of n-π^* and π–π^* transitions. Further investigation on energy band gap (E_g) values based on the UV-Vis data revealed all compounds have E_g values around 3.0 eV which makes them ideal semiconductor candidates supported with the morphologies study through SEM that showed slightly smooth surface which is preferred in thin film fabrication. CV

analysis on the other hand showed redox reaction in the range -1.5 V to +2.5 V with addition 3 mL of 0.3 M supporting electrolyte. TGA showed that all compounds have good stability under heat stress with onset degradation temperature around 300 °C while around 500 °C for the offset temperature and total degradation more than 50% from the initial weight. Based on DSC and POM analyses, the compounds without substituents showed a smectic A phase in majority (fan-shaped textures) with highest average transition temperature around 200 °C. The ones with substituents showed schlieren texture of nematic phase highest at 190 °C and 140 °C for **5a-5e** and **4a-4e** series respectively. Therefore, it is undoubtedly that the proposed molecules have displayed a good performance in liquid crystal study as well as has provided a great opportunity to explore the molecules in diverse molecular electronic applications in the future undertaking.

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SINTESIS DAN PENCIRIAN TERBITAN DWITUKAR GANTI TERKONJUGAT TERETINILASI-IMINA BERPOTENSI SEBAGAI BAHAN HABLUR CECAIR

NUR AMIRAH NABILAH BINTI MOHD RASHID

OGOS 2019

Penyelia Utama : **Profesor Madya Ts. Wan Mohd Khairul bin Wan Mohamed Zin, PhD**

Fakulti : **Fakulti Sains dan Sekitaran Marin**

Bahan hablur cecair yang umum kebiasaannya mempunyai bahagian tengah yang teguh, penghubung/jambatan dan rantaian ekor yang fleksibel. Dengan mengambil kira hal ini dengan lebih mendalam, 15 sebatian baru yang mempunyai etinil (C≡C), imina (C=N) dan rantai alkoksi telah diperkenalkan melalui proses kondensasi antara amina primer dan aldehid. Molekul-molekul yang sangat terkonjugat dengan formula umum Penderma-Ar(C=N)Ar(C≡C)Ar(C=N)Ar-Penderma dipercayai untuk menunjukkan sifat hablur cecair. Semua sebatian yang disintesis telah dicirikan secara spektroskopi dan analitikal melalui Analisis Unsur Mikro CHN, Sinar Inframerah Penukarganti Fourier (FTIR), Spektroskopi Ultra-Lembayung Sinar Tampak (UV-Vis), ^{1}H dan ^{13}C Resonans Magnetik Nukleus (NMR), Analisis Gravimetri Terma (TGA), Mikroskop Pengimbas Elektron (SEM) dan Analisis Voltametri Kitaran (CV). Untuk kajian hablur cecair, Kalorimetri Pengimbas Perubahan (DSC) dan Mikroskop Optik Terkutub (POM) dilaksanakan untuk memberikan kefahaman yang lebih baik. Spektra inframerah menunjukkan jalur dikehendaki C=N dan C≡C masing-masing pada 1617 – 1621 cm^{-1} dan 2201 – 2209 cm^{-1} yang seterusnya disahkan dengan kehadiran resonans masing-masing C=N sekitar δ_H 8.31 – 8.39 ppm dan δ_C 159.00 – 161.75 ppm dalam spektroskopi ^{1}H dan ^{13}C NMR. Peralihan elektronik $\pi-\pi^*$ yang direkodkan melalui spektroskopi UV-Vis dipercayai muncul daripada kumpulan berfungsi C=C (fenil) dan C≡C, manakala C=N dan OC_nH_{2n+1} menghasilkan campuran peralihan n-π^* dan $\pi-\pi^*$. Kajian teori yang mendalam ke atas jurang jalur tenaga (E_g) yang merujuk kepada data UV-Vis menunjukkan kesemua sebatian mempunyai nilai E_g sekitar 3.0 eV yang menjadikan

mereka calon semikonduktor yang baik dibantu oleh kajian SEM menunjukkan permukaan sedikit rata yang menjadi pilihan untuk fabrikasi filem nipis. Analisis CV pula menunjukkan tindak balas redoks di antara -1.5 V hingga +2.5 V dengan tambahan elektrolit pembantu. TGA menunjukkan semua sebatian mempunyai suhu penguraian yang tinggi dan kestabilan di bawah tekanan suhu dengan suhu penguraian permulaan sekitar 300 °C manakala 500 °C bagi suhu pengakhiran dan jumlah penguraian daripada berat awal lebih 50%. Berdasarkan analisis DSC dan POM, semua sebatian tanpa kumpulan pengganti secara keseluruhannya menunjukkan fasa smektik A (tekstur bentuk kipas) manakala sebatian yang mempunyai kumpulan pengganti menunjukkan tekstur schlieren iaitu fasa nematik pada suhu tertinggi masing-masing 190 °C dan 140 °C bagi siri **5a-5e** dan **4a-4e**. Oleh itu, adalah tidak boleh disangkalkan lagi bahawa molekul-molekul yang dicadangkan menunjukkan prestasi yang bagus dalam kajian hablur cecair, serta menyediakan pelbagai peluang untuk molekul-molekul ini dikaji secara mendalam sebagai aplikasi elektronik molekul pada masa akan datang.