Study on the Synthesis and Optoelectro Properties of Pyrimdine Containing Linear Molecules

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Abstract:

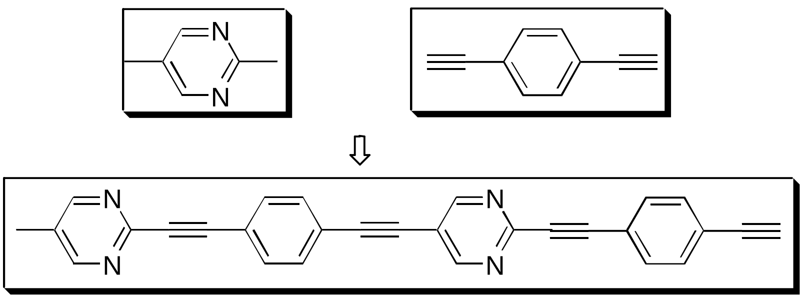
Take the advantage of different reactivity on the 2- and 5-position of 5-bromo-2-iodopyrimidine, an efficient one-pot synthetic protocol of sequential Sonogashira coupling reaction with different alkynes was established for synthesizing pyrimidine containing linear conjugated oligomers. A variety of linear oligomers with 2 pyrimidines ring were synthesized. Photophysical properties like UV-VIS and photoluminescence were measured in some of these oligomers.

[illegible]

[illegible] 5-bromo-2-iodopyrimidine [illegible] Sonogashira [illegible]

Research Background and Objectives:

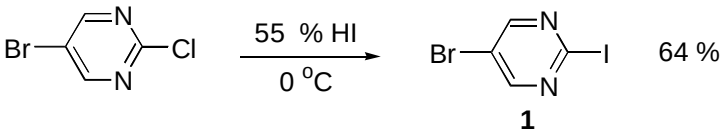
The potential use of conjugated organic oligomers as active components in optoelectronic devices has attracted a great deal of attentions in recent years. Particularly, light emitting diodes (LEDs) have been extensively studied due to their promise for practical applications(1). However, it is well known that most organic materials suitable for LEDs have smaller hole injection barriers than electron injection barriers. In order to increase the efficiency of light emitting from these devices, an excellent electron transporting organic material is highly demanding. A more practical approach for searching such materials is to find a conjugated system with lower LUMO. Thus introduced CN groups on the vinylene bridges of poly(arylenevinylenes) has resulted in an increase in the electron affinity of polymeric materials for LEDs(2). In our last NSC proposal we subjected ourselves to synthesize a new type of oligomeric materials with high electron affinity. We chose pyrimidine according to its high ability to accept electrons(3) as our candidate to incorporate into the oligomeric (1,4-phenylene)ethynylene backbone. The new-formed linear molecules then subject to evaluate its possibility of acting as an electron transporting and/or light emitting material by checking their photophysical and electrochemical properties.



Results and Discussions

1. Synthesis of pyrimidine containing linear oligomeric molecules

First of all, we slightly modified the known procedure[4] for preparation of 5-bromo-2-iodopyrimidine **1**. Well-grounded powder of 2-chloro-5-bromopyrimidine[5] was added into a cold 55% HI solution, after stirring at 0-5 °C for 12 hours, solid $NaHCO_3$ was added slowly to quench reaction carefully and followed by decolorizing with saturated Na_2SO_3 aqueous solution, extract with CH_2Cl_2 and evaporate to afford pale-yellow solid. Pure white needle crystal of 5-bromo-2-iodopyrimidine was obtained by recrystallization from hexane in 64% yield.



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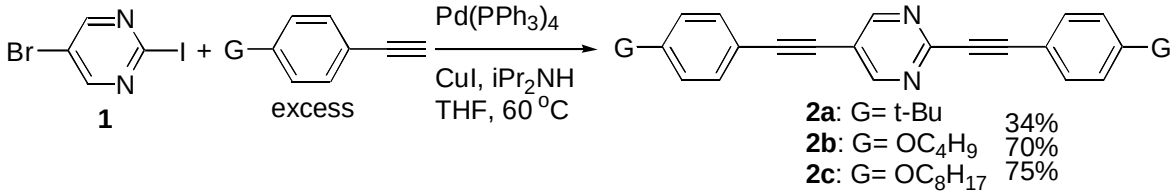
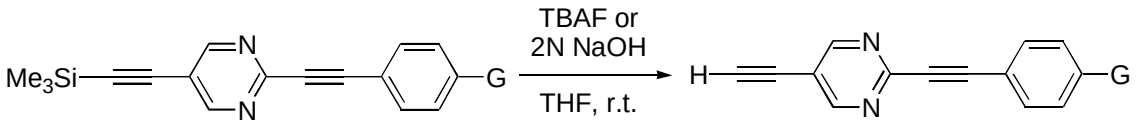
At 50 °C, Pd-catalyzed Sonogashira coupling reaction of 5-bromo-2-iodopyrimidine with excess alkynes afford bis-coupling product **2a-c** in moderate to good yields. However, at room temperature, the coupling reaction of 5-bromo-2-iodopyrimidine **1** would selectively occur only on the 2-position in the presence of a catalytic amount of $Pd(PPh_3)_4$ and excess iPr_2NH in dry THF solution, then trimethylsilylacetylene was added for the second coupling reaction on the 5-position without adding extra catalyst. The second coupling reaction was completed normally in 3 hours at 60 °C. The trimethylsilyl group was removed by adding either nBu_4NF or 2N NaOH aq. solution in THF at room temperature to give **3a-c**.

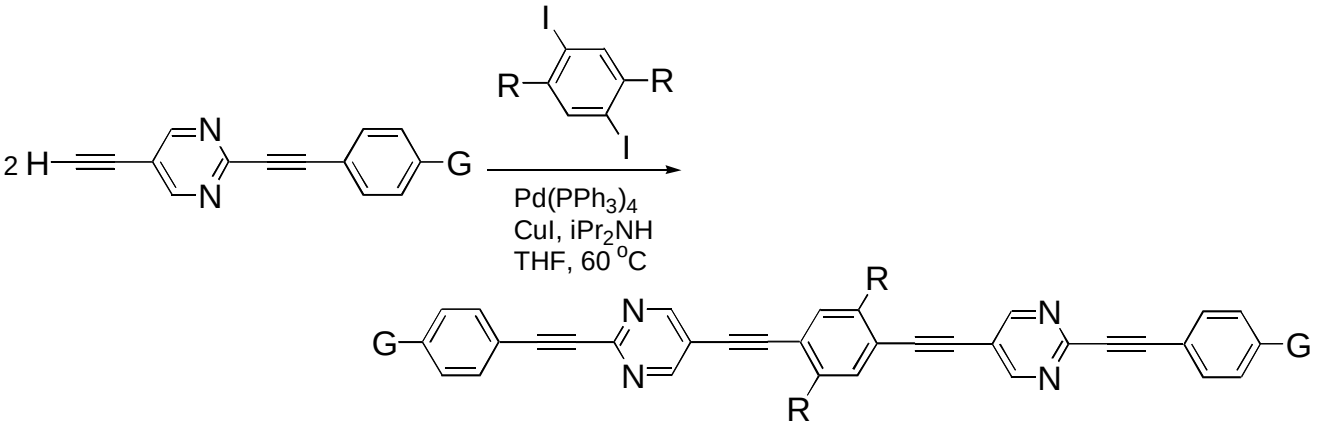


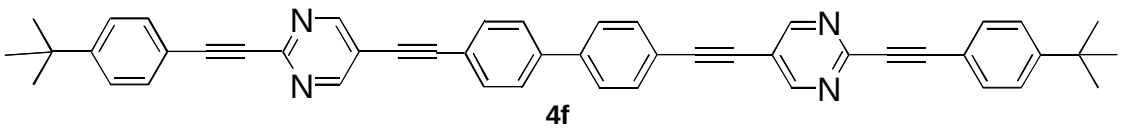
2a: G= t-Bu 34%
2b: G= OC_4H_9 70%
2c: G= OC_8H_{17} 75%



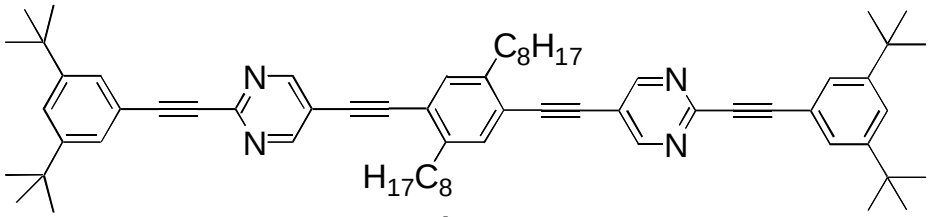
3a: G= t-Bu 50%
3b: G= OC_4H_9 64%
3c: G= OC_8H_{17} 60%

Our target linear oligomers **4a-c** with 5 aromatic rings were synthesized in excellent yields by treating compound **3a-c** with diiodoaromatic compound using our standard Sonogashira coupling reaction condition. In order to diverse our targets, different diiodoaromatic compounds for example 1,1'-diiodobipehnyl has been used as connector for **3a** to afford **4f**. Instead of **4d** and **4e** are very soluble in polar organic solvents for example CH_2Cl_2, $CHCl_3$, 1,1'-dichloroethane, 1,1',2,2'-tetrachloroethane, **4a-c** and **4f** are slightly soluble in chloroform but more soluble in 1,1',2,2'-tetrachloroethane. We are now trying to use the same synthetic strategy for synthesizing a more soluble fully alkyl-substituted linear analog **4g**.





4f



4g

2. *Photophysical Properties of Linear Molecules containing Pyrimidines*

UV-VIS absorption spectra of **2a**, **2b**, **4a**, **4c** in CHCl3 were shown in Figure 1. As the length of conjugation increases, the absorption maximum shows slightly *red shift*. Compound **2b** and **4c** with octoxyl group as substituent absorb light at longer wavelength compared with their *t*-butyl-substituted analogs **2a** and **4a**. Upon UV excitation, the photoluminescence spectra of **2a, 2b, 4a, 4c,** are shown in Figure 2. The maximum wavelength of emissions was observed with slightly red shift as the length of conjugation increased. The same substituent effect as observed in UV-VIS spectra was also obtained in emission spectra. Compound **2b** and **4c** with octoxyl group as substituent emit blue light with longer wavelength compared to their *t*-butyl-substituted analogs **2a** and **2b**. Compound **4a** with blue fluorescent emission maxima at 397 nm and 418 nm in different concentrations is shown in Figure 3. Both emissive intensities are concentration-dependent. The emissive intensity at 397 nm decreased as the concentration increased. Whereas, the intensity of emission at 418nm increased as the concentration increased. The changes of the relative intensities of these two peaks could be attributed to the formation of excimer. Thus, the self-quenching effect of **4a** was observed at relatively high concentration (7.5×10^{-5} M). The photoluminescent spectrum of **4c** with different concentration is also shown in Figure 4.

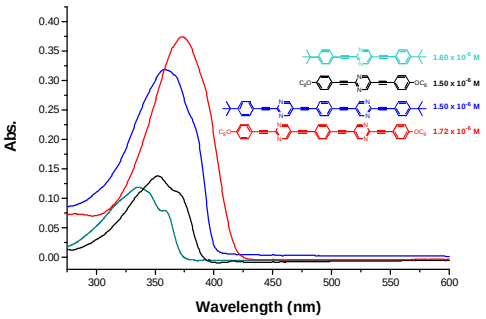


Figure 1. UV-VIS Spectra

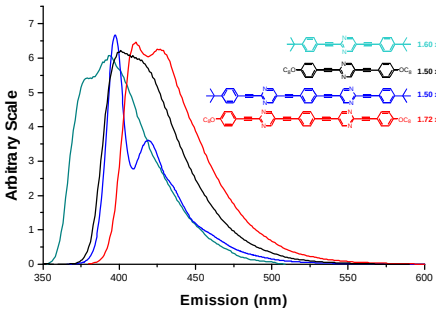


Figure 2. Photoluminescence

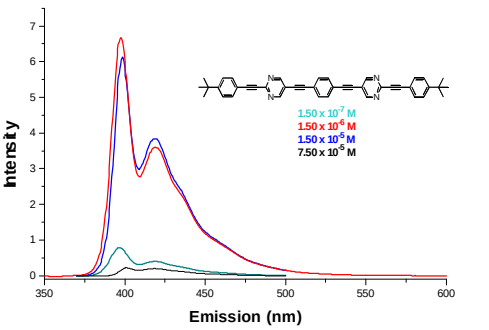


Figure 3. Concentration Dependent Photoluminescence

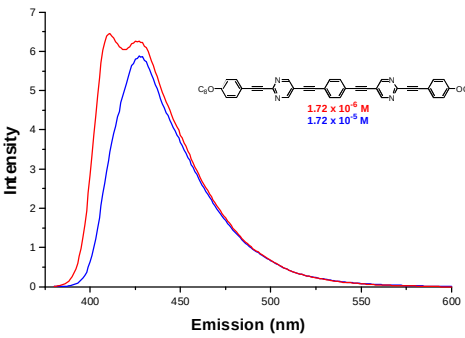


Figure 4. Concentration Dependent Photoluminescence

Self-Evaluation

In our last NSC proposal, we set our first goal to develop an efficient synthetic strategy for synthesizing pyrimidine containing linear conjugated oligomers. According to this progress report, take the advantage of different reactivity on the 2- and 5-position of 5-bromo-2-iodopyrimidine, we have already established an one-pot synthetic protocol of sequential Sonogashira coupling reaction with different alkynes. A variety of linear oligomers with 2 pyrimidines ring were synthesized very efficiently. We set our second goal to study the photophysical and electrochemical properties of these oligomers. All measurements now are undergoing in order to evaluate the possibility for applications as an electron transporting and/or light emitting materials in organic LEDs.

References

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[2] (a) Greenham, N. C.; Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *Nature*, **1993**, *365*, 628. (b) Moratti, S. C.; Cervini, R.; Holmes, A. B.; Baigent, D. R.; Friend, R. H.; Greenham, N. C.;Gruner, J.; Hamer, P. J. *Synth. Met.* **1995**, *71*, 2117. (c) Peng, Z.; Galvain, M. E. *Chem Mater.* **1998**, 1785.

[3] Gommper, R.; Mair, H. –J.; Polborn, K. *Synthesis*, **1997**, 696.

[4] Goodly, J. W.; Hird, M.; Lewis R. A.; Toyne, K. J. *Chem. Commun.* **1996**, 2719.

[5] Which is synthesized from bromination of 2-hydroxypyrimidine hydrochloride with Br_2 followed by chlorination on the 2-position with $POCl_3$