Synthesis of Core Substituted Napthalenediimides for n-Type Organic Semiconducting

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Abstract:

The lack of stable high performance organic n-type semiconductors is a major challenge for the field. We explored one possibility for creating such a material by further augmenting previously successful *N,N'*-bis(cyclohexyl) napthalenediimide with a novel core extension. The synthesized mono- and bis-core-extended bis(cyclohexyl) napthalenediimides were given to a collaborating group to measure the compound's electronic properties.

Introduction:

Effective organic semiconductors are highly desirable in industry because organics, unlike silicon, are generally elastic and can be deposited with relatively simple solution chemistry techniques, thus allowing for flexible electronics devices and inexpensive roll to roll manufacturing. Semiconductor performance for thin film, field effect transistors is quantified through field effect mobility (FET), which is defined as the average charge carrier (hole or electron) drift velocity per unit electric field. Semiconductors can be considered high performance if they have a FET greater than that of amorphous silicon, which is 1 $cm^2\ V^{-1}\ s^{-1}$.

One of the major challenges in the field of organic semiconductors today is the lack of n-type organic semiconductors that can match the performance of their p-type counterparts [1].

Previous research has demonstrated that the use of cyclohexyl imides dramatically improves the FET of naphthalenetetracarboxylic diimide (NDI), a widely studied and attractive organic n-type semiconductor candidate, to near 6 $cm^2\ V^{-1}\ s^{-1}$ as compared to 0.16 $cm^2\ V^{-1}\ s^{-1}$ for its straight chain hexyl counterpart [2], though issues with stability in air still remain [1]. Recently core substitution has emerged as a powerful tool to improve the stability and tune the electronic properties for NDIs [3]. Our lab has had previous success with core expansion using alkynyl groups [4].

Our research goal was to combine these results by synthesizing core-extended cyclohexyl NDIs.

Synthesis:

The synthetic scheme is outlined in Figure 1. For step one, a mixture of unsubstituted, monobromo-, and dibromo-1,4,5,8-naphthalenetetracarboxylic acid anhydride was reacted with cyclohexamine in acetic acid at reflux for one hour. After the reaction, the resultant precipitate was filtered through a Buchner funnel, washed with methanol and left to dry in the vacuum oven overnight. The dry precipitate was separated using silica gel liquid column chromatography with chloroform as the solvent. Fractions for unsubstituted, monobromo-, and dibromo- cyclohexyl NDI were collected separately.

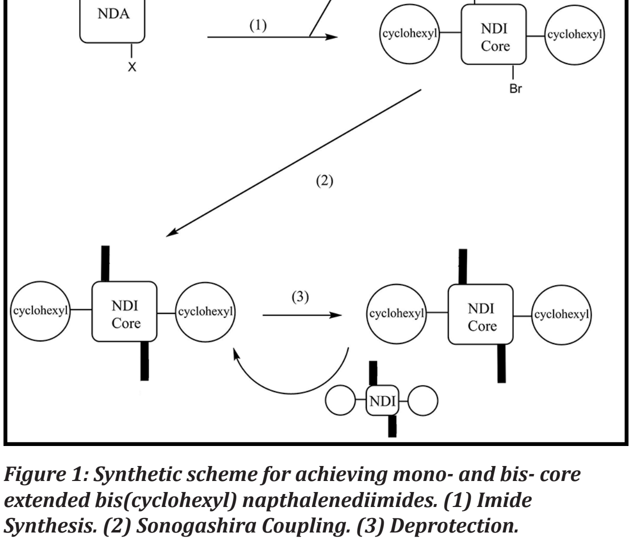

Figure 1: Synthetic scheme for achieving mono- and bis- core extended bis(cyclohexyl) napthalenediimides. (1) Imide Synthesis. (2) Sonogashira Coupling. (3) Deprotection.

For step two, the monobromo- and dibromo- fractions were each separately coupled with an alkynyl reagent with a protecting group through a palladium (II) bis(triphenylphosphine) dichloride and copper (I) iodide catalyzed Sonogashira coupling in dry and degassed tetrahydrofuran and diisopropylamine at 37°C for 16 hours. The product solution was filtered through sodium sulfate and celite. Solvent was removed with a rotary evaporator then the product was left to dry in the vacuum oven for two hours. The dry product was purified using silica gel liquid column chromatography with chloroform as the solvent.

Finally, for step three, the protection group was removed from the core extension moieties of the bis-core-extended fraction by using a deprotecting reagent. After the reaction, the organic solvent was evaporated with the rotary evaporator, and dried in the vacuum oven overnight. The dry product was purified twice using silica gel liquid column chromatography with chloroform as the solvent. Any fractions with the protecting groups still present were recycled. There was insufficient time to perform this step on the mono-core-extended fraction.

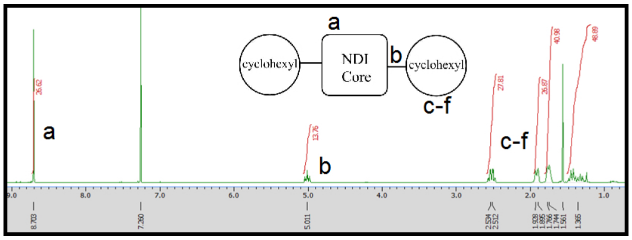

Figure 2: 1H NMR (CDCl$_3$, 400 MHz) spectrum of N,N'-*bis(cyclohexyl) napthalenediimide.*

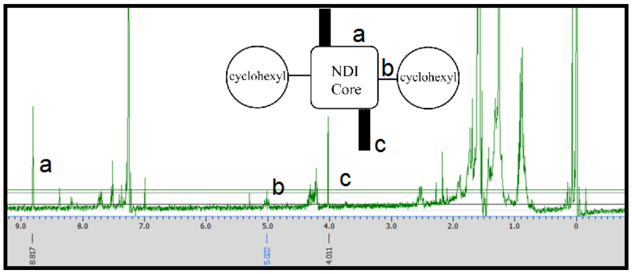

Figure 3: 1H NMR (CDCl$_3$, 400 MHz) spectrum of bis-core-extended N,N'-*bis(cyclohexyl) napthalenediimide. Full assignment impossible because impurity obscures aliphatic region.*

Results:

200 mg of unsubstituted cyclohexyl NDI were obtained as a byproduct from reaction step one to be used as a control. This product's ^{1}H nuclear magnetic resonance (NMR) in deuterium chloroform (CDCl$_3$) spectrum with peaks assigned is presented in Figure 2.

73 mg of bis-core-extended cyclohexyl NDI were synthesized. This product produced the expected peak in the mass spectrometer. This product's ^{1}H NMR in CDCl$_3$ spectrum, presented in Figure 3, has the expected aromatic (8.82 s 2H) peak, however the absence of the clear pattern visible in the aliphatic region of Figure 2 indicates the presence of impurities.

Additionally, 50 mg of protected bis-core-extended cyclohexyl NDI (^{1}H NMR in CDCl$_3$: 8.74 s 2H, 5.01 t 2H, 2.52 q 4H, 1.91 q 4H, 1.76 q 6H, 1.37 m 6H, 0.37 s 18H) and 40 mg of protected mono-core-extended cyclohexyl NDI (^{1}H NMR in CDCl$_3$: 8.69 m 3H, 5.01 t 2H, 2.52 q 4H, 1.91 q 4H, 1.76 q 6H, 1.37 m 6H, 0.37 s 9H) were synthesized, but did not have synthetic step three performed on them due to lack of time.

Future Work:

After performing synthetic step three on the mono substituted fraction and more thoroughly purifying both target compounds, the target compounds will need to have their presence further confirmed using ^{13}C NMR and have their crystal structure characterized through x-ray diffraction and atomic force microscopy. Collaborators will then measure the FET of organic thin film constructed with the target compounds and the unsubstituted control.

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References:

[1] Shan, B.; Miao, Q. Tetrahedron Lett. 2017, 58(20), 1903-1911.

[2] Shukla, D; Nelson, SF; Freeman, DC; Rajeswaran, M; Ahearn, WG; Meyer, DM; Carey, JT. Chem. Mater. 2008, 20(24), 7486-7491.

[3] Kobaisi, M. A.; Bhosale, S. V.; Latham, K.; Raynor, A. M.; Bhosale, S. V. Chem. Rev. 2016, 116, 11685-11796.

[4] Takai, A.; Takeuchi, M. submitted.