Group 14 effects in alkynyl acene small molecule semiconductors

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Abstract— **Silyl ethynyl groups have become commonplace in functionalizing organic semiconductors, where they improve solubility and stability. The identity of the side chain also dictates the molecular organization in the solid state, and thus heavily influence bulk material properties such as charge mobility. Germanium-containing side chains show the same propensity to form favorable solid state packing motifs, but carbon analogs remain mostly unexplored. Here we present a general synthesis of carbon alkynes, changes in molecular properties of acenes functionalised with these alkynes, and a rich variety in crystal packing motifs that have rarely been observed with silicon or germanium side chains.**

I. INTRODUCTION

Silyl ethynyl groups have been used extensively to provide small molecule organic semiconductors with solubility for enhanced device processing and improved stability against photoinduced oxidation and dimerization.[1]–[5] The size of the trialkylsilyl group can also be exploited for crystal engineering, steering the optoelectronically active polycyclic aromatic hydrocarbons into intermolecular arrangements beneficial for charge transport or optical effects in the solid state.[6] In addition to the physical size of the silyl group, attractive and repulsive non-covalent interactions involving these solubilizing groups affect the solid state packing, and therefore the bulk material properties.[7] Replacing the silicon atom by germanium results in broadly similar packing, although polymorphism has been observed for germyl pentacenes.[8] To discover more about solid state packing effects, we have synthesized all-carbon equivalents to these alkynyl substituents, and attached to a number of acene materials (Figure 1). This simple substitution affects both single molecule properties and solid-state packing arrangements, which are explored through computational analysis to learn more about the non-covalent interactions binding these small molecules together.

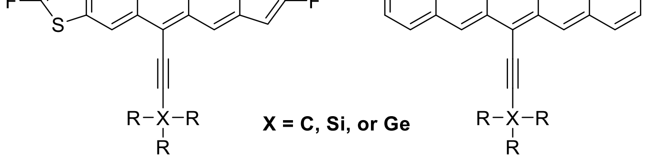
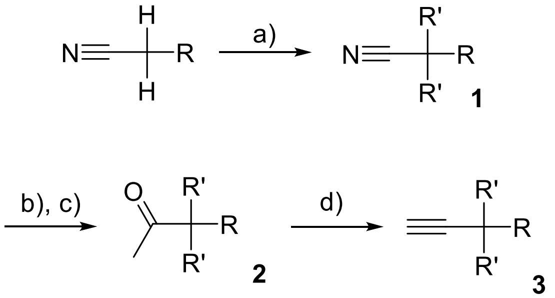


Figure 1. Structures of ethynyl acenes bearing carbon, silicon or germanium based side chains

II. SYNTHESIS & PROPERTIES OF NEW MATERIALS

A general synthetic scheme was developed to access alkynes made only of carbon and hydrogen, with tertiary alkyl substituents. In the case where all three alkyl chains are equivalent, acetonitrile can be deprotonated and alkylated three times in a one-pot procedure. Asymmetric substituents can be obtained by using commercially available alkyl nitriles, and using the one-pot procedure to include two new alkyl chains. After alkylation, nitrile **1** could be converted to a methyl imine by addition of MeLi, which could then be hydrolysed to the ketone **2** under mild conditions. Decomposition of the imine and/or ketone was observed under more acidic conditions. Finally, a chlorination / elimination protocol[9] was used to yield the alkyne, which could be attached to acene cores using well-known reaction conditions.[1]



Scheme 1. General synthetic route to all-carbon alkynes which can be attached to small molecule organic semiconductors

A. Single Molecule Properties

The replacement of silicon by carbon induced quite significant changes to single molecule properties. The HOMO and LUMO energies are raised by 0.1 and 0.15 eV respectively,

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and the optical gap is widened with absorption maxima shifted by > 10nm. Even more surprising is that germanium substituents lie between the carbon and silicon analogs, so a clear trend down group 14 is not observed. Literature precedence on the differences between these elements suggests that silicon and germanium provide electron withdrawing effects by accepting electrons into empty d orbitals.[10], [11] Our computational analysis on the acene derivatives and model phenyl compounds suggests that a) carbon substituents can similarly accept electrons by resonance into both empty p- and d-orbitals, and b) that these effects are extremely small for germanium due to longer C-Ge bonds and mismatched orbital size and energy. Instead, hyperconjugation[12] is a major factor in determining the electron donating / withdrawing effects in this series. Carbon substituents have a strong electron donating hyperconjugation effect, while silicon and germanium have a stronger withdrawing than donating effect, with silicon being the most withdrawing. This serves to lower the energy levels of the silylated acenes and red-shift their absorption.

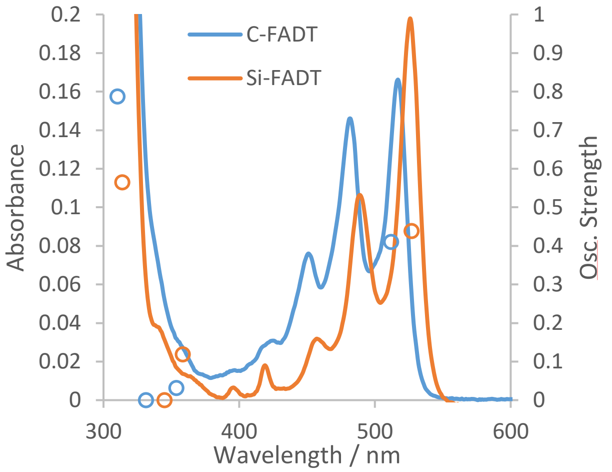

Figure 2. Solution absorption spectra of difluoro-anthradithiophenes where X = C (blue) or Si (orange). Dots represent TD-DFT (tuned ωB97XD/6-31G* in $CHCl_3$ PCM) calculated excitations.

III. SOLID STATE PACKING

The packing of the acene molecules is important to the bulk material properties, where orbital overlap between adjacent molecules is required for charge transport through the material. For substituted acenes, the desirable 2D brickwork packing motif provides multiple routes for charges to travel through the material, which may help to lessen the effects of static and dynamic disorder, and grain boundaries within thin films. A number of silyl derivatives have achieved this packing, using the size and stabilising forces between the alkyl chains to dictate the assembly of the molecules. We have synthesized a number of different side chains consisting only of carbon and hydrogen to try to achieve the similar packing, and to then investigate if there are any other effects that may arise from this atomic substitution. In most cases, we were able to grow single crystals that were suitable for x-ray diffraction to reveal the intermolecular arrangements. Thus far the desired 2D brickwork has remained elusive, but a number of intriguing packing motifs have been found.

Experimental crystal structures reveal 1D pi stacking arrangements commonplace with the silyl substituents, but also some 1D brickwork packing, where the full 2D nature of the brickwork pattern is not fully realized. This can in part be explained by the asymmetry of the side chains. As a sort of hybrid between a 1D slip stack and 2D brickwork arrangement, these novel packing structures may prove very interesting to investigate the role of dimensionality in solid-state charge or exciton transport.

To further investigate the origin of the packing, we have also studied the solid-state structures *in silico*, using plane wave density functional theory to optimise unit cell geometries, and symmetry adapted perturbation theory (SAPT0) to investigate intermolecular non-covalent interactions. As well as the new experimental structures, we have also created hypothetical 2D packing by adapting the crystal structure of TES-FADT or TIPS-PN with the different side chains that we have synthesized.

Comparison of SAPT0 energies reveals that packing is affected by a difference in size of the side chains, due to elongated Si-C bonds in comparison to C-C ones. There are also differences in electron density upon descending group 14, which influences the attractive dispersion forces as well as the repulsive exchange energies. Finally, where X = Si or Ge, the C-X bonds become polarised due to differences in electronegativities. These slightly polar bonds also affect the non-covalent interactions through the increased electrostatic energies observed in SAPT analysis.

IV. CONCLUSIONS

Organic semiconductors bearing alkynyl substituents made of only carbon and hydrogen have been synthesized, and compared to their analogs with other group 14 elements (Si and Ge). The atomic substitution impacts the optoelectronic properties of the single molecules by electron donating / withdrawing effects, particularly by the often-ignored hyperconjugation mechanism. The side chain substitution also directly impacts the solid-state packing, which in turn is expected to strongly influence the bulk material optoelectronic properties courtesy of intermolecular orbital overlap. While we have not yet arrived at a true two-dimensional brickwork pattern sought after for transistor devices, some derivatives show very interesting packing. By studying a range of molecular packing motifs realized by the carbon side chains, we are also in turn learning more about the cohesive forces that bind silyl and germyl functionalized organic semiconductors in the solid state.

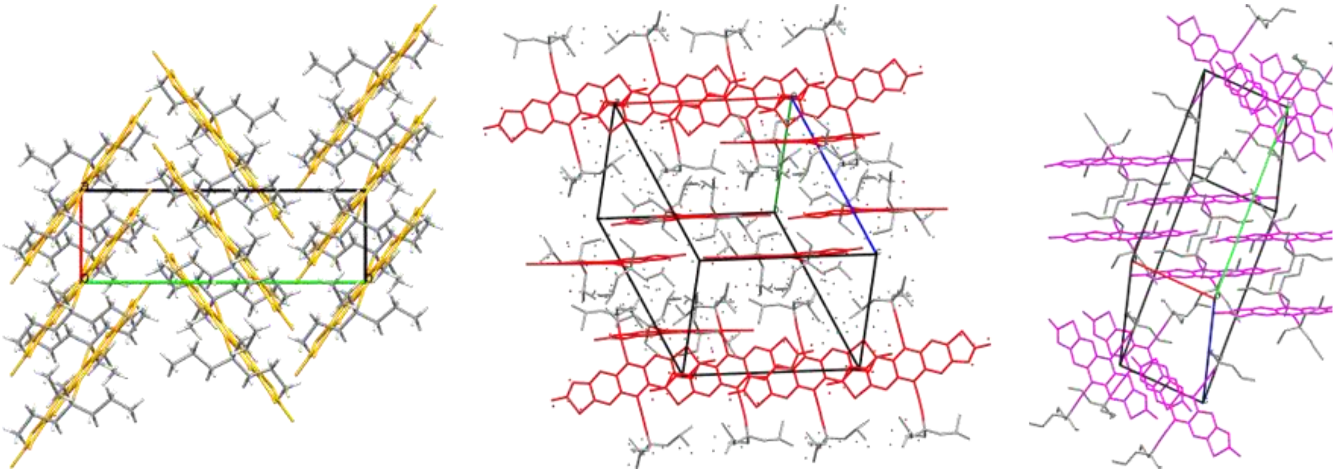

Figure 3. Examples of crystal packings obtained with all carbon side chains, from 1D slip stack (left) to 1D brickwork (middle and right). Acene cores are highlighted in different colors, and side chains in grey.

ACKNOWLEDGMENT

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REFERENCES

[1] J. E. Anthony, J. S. Brooks, D. L. Eaton, and S. R. Parkin, “Functionalized Pentacene: Improved Electronic Properties from Control of Solid-State Order,” *J. Am. Chem. Soc.*, vol. 123, no. 38, pp. 9482–9483, 2001.

[2] D. T. Chase *et al.*, “Electron-accepting 6,12-diethynylindeno[1,2-b]fluorenes: synthesis, crystal structures, and photophysical properties.,” *Angew. Chem. Int. Ed. Engl.*, vol. 50, no. 47, pp. 11103–6, Nov. 2011.

[3] L. Zhang *et al.*, “Bistetracene: an air-stable, high-mobility organic semiconductor with extended conjugation.,” *J. Am. Chem. Soc.*, vol. 136, no. 26, pp. 9248–51, Jul. 2014.

[4] W. Fudickar and T. Linker, “Why triple bonds protect acenes from oxidation and decomposition.,” *J. Am. Chem. Soc.*, vol. 134, no. 36, pp. 15071–82, Sep. 2012.

[5] L. Zhang *et al.*, “Tri-isopropylsilylethynyl-Functionalized Graphene-Like Fragment Semiconductors: Synthesis, Crystal Packing, and Density Functional Theory Calculations,” *Chem. – A Eur. J.*, vol. 19, no. 52, pp. 17907–17916, 2013.

[6] J. E. Anthony, D. L. Eaton, and S. R. Parkin, “A Road Map to Stable, Soluble, Easily Crystallized Pentacene Derivatives,” *Org. Lett.*, vol. 4, no. 1, pp. 15–18, Jan. 2002.

[7] K. J. Thorley, T. W. Finn, K. Jarolimek, J. E. Anthony, and C. Risko, “Theory-Driven Insight into the Crystal Packing of Trialkylsilylethynyl Pentacenes,” *Chem. Mater.*, vol. 29, no. 6, pp. 2502–2512, Mar. 2017.

[8] J. C. Sorli *et al.*, “Impact of Atomistic Substitution on Thin-Film Structure and Charge Transport in a Germanyl-ethynyl Functionalized Pentacene,” *Chem. Mater.*, vol. 31, no. 17, pp. 6615–6623, Sep. 2019.

[9] B. Stulgies *et al.*, “Six- and Eightfold Palladium-Catalyzed Cross-Coupling Reactions of Hexa- and Octabromoarenes,” *Chem. Eur. J.*, vol. 11, no. 1, pp. 308–320, Jan. 2005.

[10] A. J. Fleisher, C. D. Schaeffer, B. A. Buckwalter, and C. H. Yoder, “1H,13C, and73Ge NMR spectral analysis of substituted aryltrimethylgermanes,” *Magn. Reson. Chem.*, vol. 44, no. 2, pp. 191–194, Feb. 2006.

[11] A. N. Egorockkin, S. E. Skobeleva, and T. G. Mushtina, “The first ionization potentials and conjugation in benzene derivatives containing organosilicon, organogermanium, organotin, and organolead substituents,” *Russ. Chem. Bull.*, vol. 46, no. 1, pp. 65–70, 1997.

[12] A. N. Egorochkin, G. A. Razuvaev, and M. A. Lopatin, “Hyperconjugation in phenyl and benzyl derivatives of the main group IV elements,” *J. Organomet. Chem.*, vol. 344, no. 1, pp. 49–60, Apr. 1988.