

Crosslinkable 3,4-Furan containing organic semiconductors

By: Robert B. Login

I wanted to figure out how to crosslink organic semiconductors(OS) without disrupting their conjugation but not through the conventional use of crosslinkable pendant R groups (crosslinkable pendant groups after crosslinking would obviously retain OS conjugation).

Crosslinking is considered a method to stabilize OS film configurations and is a very active pursuit in OS chemistry and has been recently reviewed:

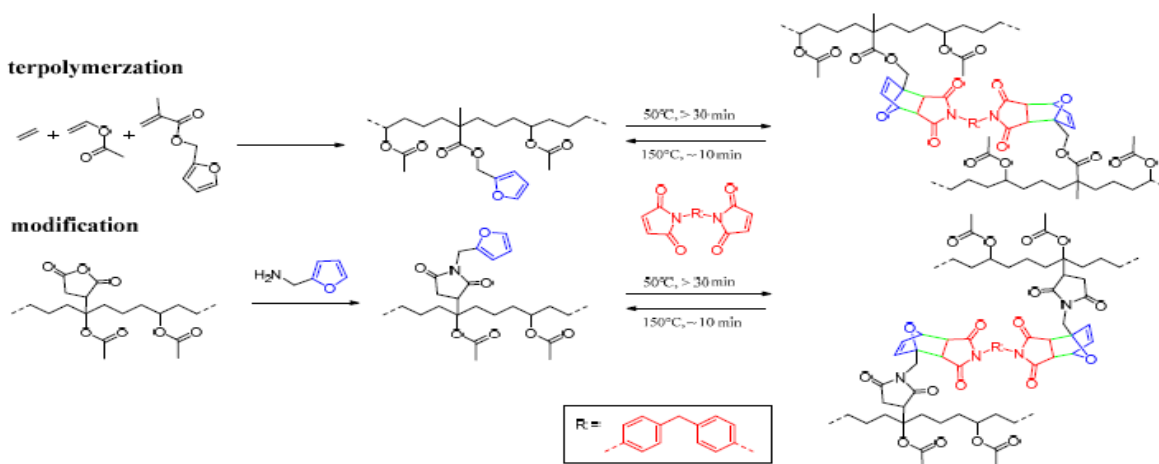
Kahle, Frank-Julian, et al. "Crosslinked Semiconductor Polymers for Photovoltaic Applications." *Advanced Energy Materials*, 7.16 (2017).

“Organic solar cells (OSCs) have achieved much attention and meanwhile reach efficiencies above 10%. One problem yet to be solved is the lack of long term stability. Crosslinking is presented as a tool to increase the stability of OSCs. A number of materials used for the crosslinking of bulk heterojunction cells are presented.”

Patel, Dinesh G. Dan, Kenneth R. Graham, and John R. Reynolds. "A Diels–Alder crosslinkable host polymer for improved PLED performance: the impact on solution processed doped device and multilayer device performance." *Journal of Materials Chemistry*, 22.7 (2012): 3004-3014.

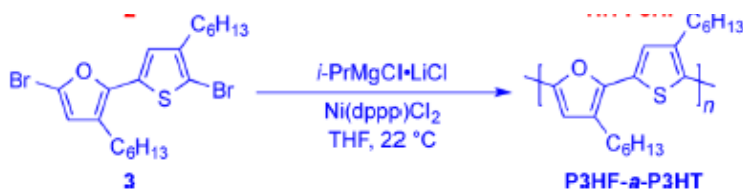
“We report on the synthesis of a polyfluorene derivative, **PFO(X)**, with furan pendant groups capable of Diels–Alder crosslinking with a maleimide containing small molecule passive crosslinker (**PC**) and a maleimide containing red emitting donor–acceptor–donor dopant molecule, **bE-BTD(X)**.”

Although not related to OS polymers the following scheme is suggestive of my proposal and the DA crosslinking chemistry that was also employed in the Patel ref. above.



Rubber with Bismaleimide."Polymers", 9.3 (2017): 81.

Furan can be copolymerized with other monomers usually employed in OS chemistry as illustrated in the following references:

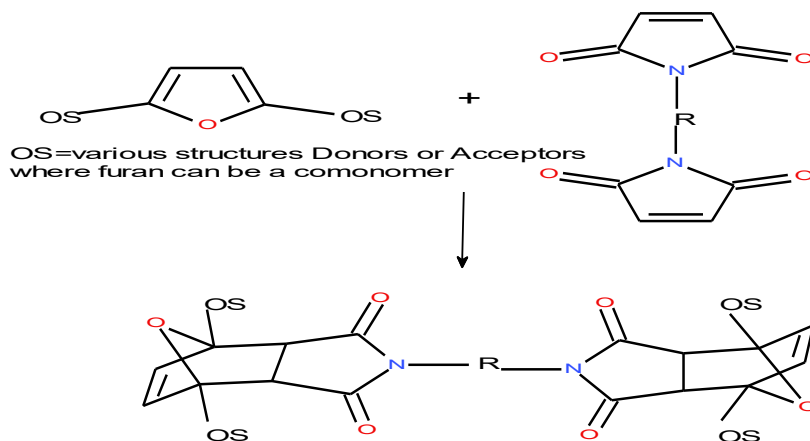


Qiu, Yunyan, et al. "Synthesis of Polyfuran and Thiophene-Furan Alternating Copolymers Using Catalyst-Transfer Polycondensation." *ACS Macro Letters*, 5.3 (2016): 332-336.

Woo, Claire H., et al. "Incorporation of furan into low band-gap polymers for efficient solar cells." *Journal of the American Chemical Society*, 132.44 (2010): 15547-15549.

Korshin, Edward E., Gregory M. Leitus, and Michael Bendikov. "Convenient access to readily soluble symmetrical dialkyl-substituted α -oligofurans." *Organic & biomolecular chemistry*, 12.34 (2014): 6661-6671.

The Diels Alder(DA) reaction of 2,5 substituted (polymer containing) furans leads to loss of the conjugation of the OS. However, the DA reaction with maleimides is thermally reversible. Therefore said furan containing OS polymers can be crosslinked with bismaleimides to fix the polymer morphology which could then be reversed during the high temperature annealing that is usually performed as a finishing step in several thin film OS applications.



Scheme 1: As can be seen the DA disrupts furan aromaticity and OS conjugation. As indicated above, this DA reaction is thermally reversible which would reestablish said conjugation. Except for the Patel ref., I haven't found a reference to the idea of having furan as part of the OS backbone conjugation and its DA reaction, even though the literature of "healable polymers" based, on reversible DA, uses this chemistry.

Polgar, L. M., et al. "Use of Diels–Alder Chemistry for Thermoreversible Cross-Linking of Rubbers: The Next Step toward Recycling of Rubber Products?." *Macromolecules*, 48.19 (2015): 7096-7105.

Craven, James M. "Cross-linked thermally reversible polymers produced from condensation polymers with pendant furan groups cross-linked with maleimides. U.S. Patent No. 3,435,003. 25 Mar. 1969.

Aromatic derivatives:

The above DA reaction products can be subsequently treated with certain acids to form the corresponding aromatic imide. This would be a unique way of placing an acceptor moiety in OS backbones(see scheme 2 E).

Patet, Ryan E., et al. "Kinetic regime change in the tandem dehydrative aromatization of furan Diels–Alder products." *ACS Catalysis*, 5.4 (2015): 2367-2375.

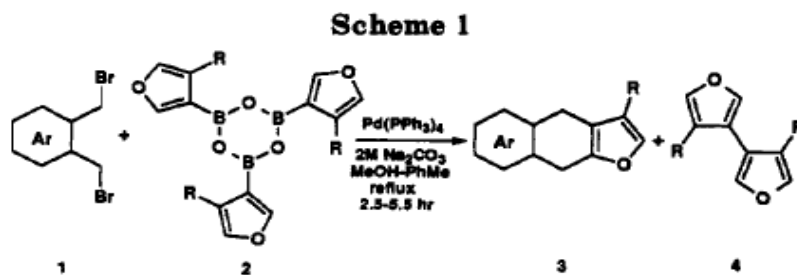
Song, Song, et al. "Diels–Alder and dehydration reactions of furan derivatives with ethylene catalyzed by liquid Brønsted acids and Lewis acids." *Journal of Molecular Catalysis A: Chemical*, 420 (2016): 134-141.

3,4 Furan Copolymers:

First let me review how said monomers have been synthesized. Furans coupled at the 2,5 positions are the standard for polymerization. Recently Cao and Rupar reviewed the current usual 2,5-coupling situation in an excellent review.

Cao, Hongda, and Paul A. Rupar. "Recent Advances in Conjugated Furans." *Chemistry-A European Journal*, 23.59 (2017): 14670-14675.

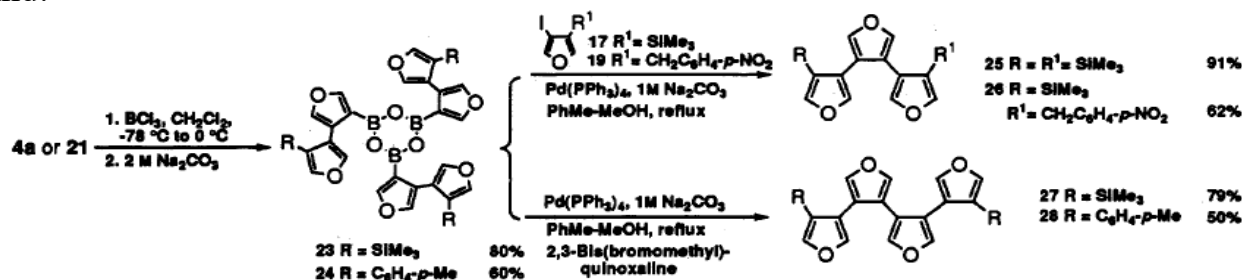
There are very few references to coupling through the 3,4-Furan positions. In fact they are all based on Prof. H. Wong's et. al. work concerning their synthesis.



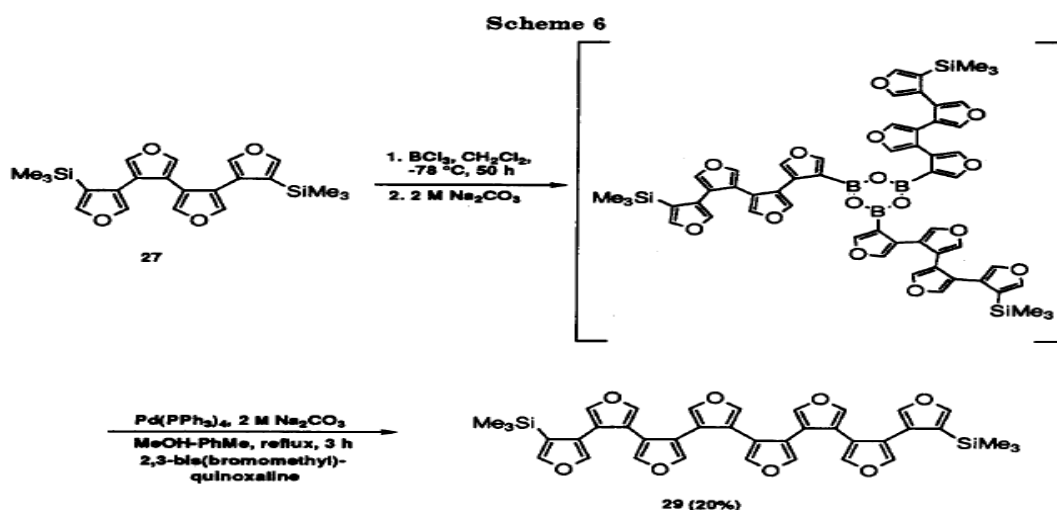
The organoboroximes are prepared from Bf_3 . When certain auxiliary dibromide derivatives are employed in this reaction, only 4 is produced.

6		R = SiMe ₃ 2a	3 above (0) % yield	4 %yield R = SiMe ₃ 4a (87)
7		R = SiMe ₃ 2a	(0)	R = SiMe ₃ 4a (90)

And:



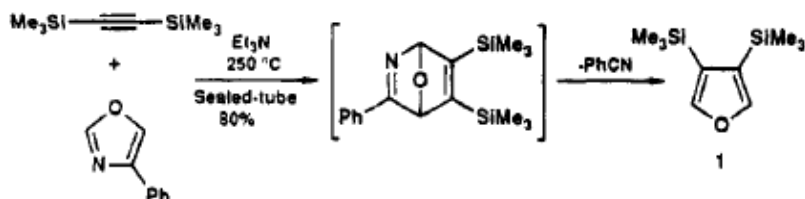
Also:



Song, Zhi Zhong, and Henry NC Wong. "Regiospecific synthesis of furan-3, 4-diyl oligomers via palladium-catalyzed self-coupling of organoboroxines." *The Journal of Organic Chemistry*, 59.1 (1994): 33-41.

However, the 3,4-bis (trimethylsilyl) furan would be the simplest to incorporate into OS's.

Scheme 1. Preparation of 3,4-Bis(trimethylsilyl)furan



Song, Zhi Zhong, Mei Sing Ho, and Henry NC Wong. "Regiospecific synthesis of 3, 4-disubstituted furans. 7. Synthesis and reactions of 3, 4-bis (trimethylsilyl) furan: Diels-Alder cycloaddition, Friedel-Crafts acylation, and regiospecific conversion to 3, 4-disubstituted furans." *The Journal of Organic Chemistry*, 59.14 (1994): 3917-3926.

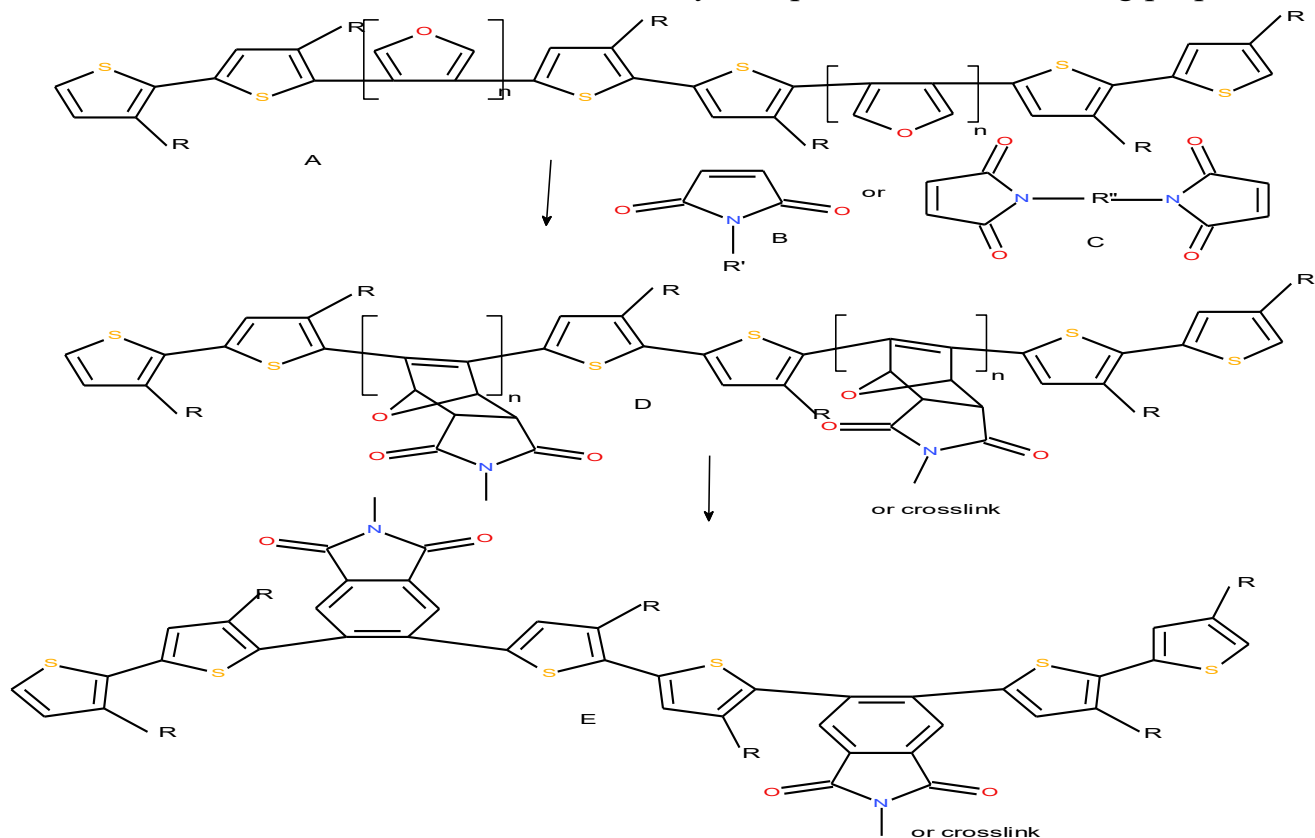
A very nice review of the above chemistry is:

Keay, Brian A. "Synthesis of multi-substituted furan rings: the role of silicon." *Chemical Society Reviews*, 28.4 (1999): 209-215.

TMS derivatives can be coupled to (hetero)aromatics with the Hyama coupling reaction.

Sore, Hannah F., Warren RJD Galloway, and David R. Spring. "Palladium-catalysed cross-coupling of organosilicon reagents." *Chemical Society Reviews*, 41.5 (2012): 1845-1866.

The above introduction is intended to facilitate your opinion of the following proposals.



Scheme 2: 3,4-furan containing OS polymers or compounds and proposed chemistry. N=1 but could be more as suggested by the above Wong references.

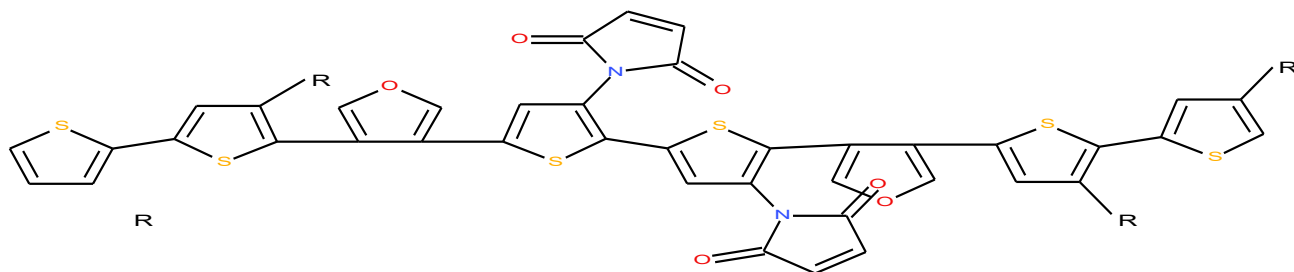
Compound A with furan attached at the 3,4 position would not be expected to exhibit good conjugation because in the 2,5 position, a quinoidal resonance is possible which is not possible with 3,4 coupling. This doesn't mean there is no conjugation; however, with a DA reaction, a double bond would result which would exhibit excellent conjugation and might be a driving force for said DA reaction.

Both B and C maleimides can be tuned depending on the nature of the R groups. For example the R groups can be derivatized with various amines, carboxylates, halogens etc.. C crosslinkers would result in a gel if water soluble functionalities were also associated with the crosslinker. Quaternary derivatives associated with photo active OS groups might be a route to biocidal products.

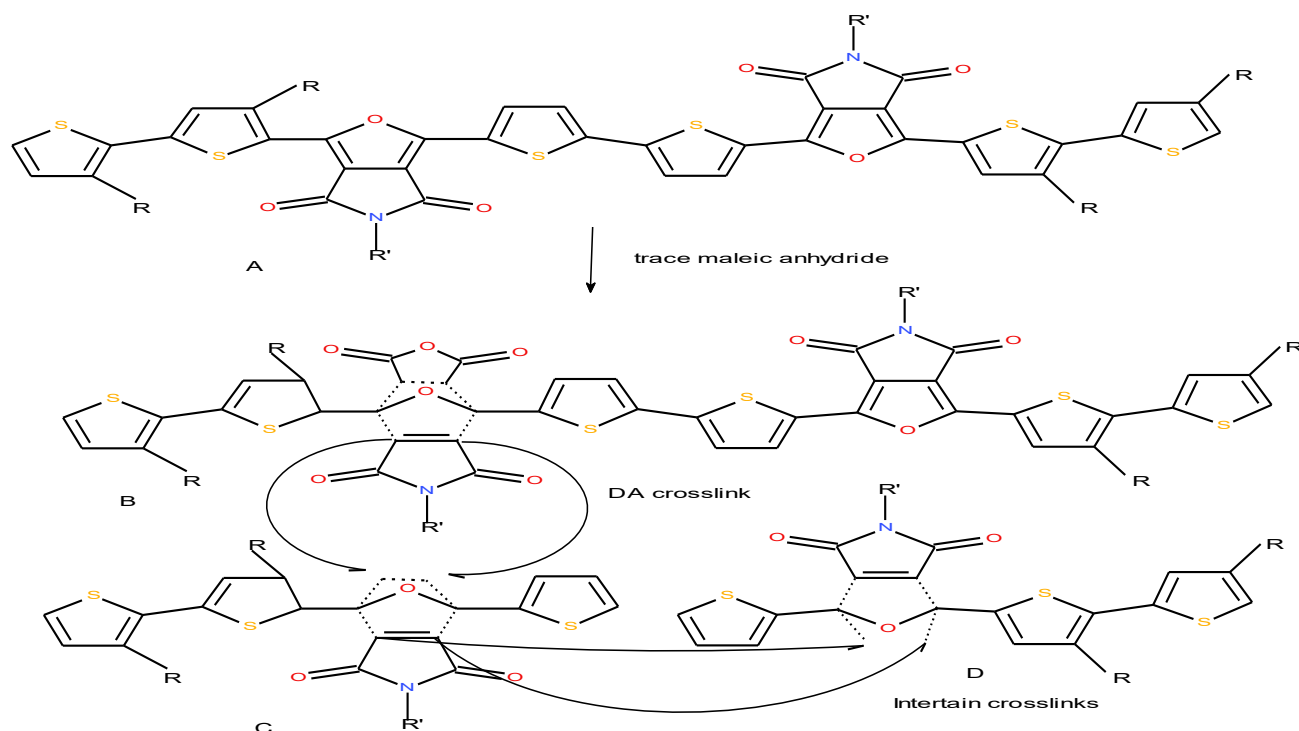
Scheme 2 illustrates copolymers with thiophenes but this is just one possible example.

This chemistry could be possible with numerous OS as long as the 3,4 furan can be included in the OS backbone. Therefore, these copolymers or small molecule compounds can be reversibly crosslinked, or derivatized with Diels-Alder dieneophiles which can be further transformed into benzene maleimide or other derivatives.

The thiophene repeat monomers can be 3-amino derivatized and subsequently condensed with maleic anhydride.



Scheme 3: Here, the maleimides are as close to the OS backbone as possible should closer distance between chains be desired or results in improved OS performance. I'm just showing a simple example for instructive purposes. The maleimide can obviously be attached to both donor and/or acceptor OS's. These derivatives would react by the DA reaction to form reversible crosslinks. This maybe a way to control OS morphology either permanently or temporarily. Furthermore the DA adduct can be converted to benzomaleimide derivatives. I would also point out that other dieneophiles can be employed that can also be attached to the OS backbone instead of the illustrated maleimide.



Scheme 4: 5-methylfuro[3,4-c]pyrrole-4,6-dione or other R groups can be initiated with a

dieneophiles like maleic anhydride to then chain react by DA crosslink reactions. Further more the bicyclo can be further transformed into a benzene derivative.

Also this crosslinking DA chain reaction results in very little impurities, only the small amount of maleic anhydride initiator that would be required.

Thank you for reading these proposals! Please give me some feedback, corrections, comments etc.

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