Polymeric Isoindigo, benzodifurandione and benzodipyrrolediones
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With the following proposals, I continue my interest in lactam containing organic semiconductors with another example of proposals based on isoindigo related chemistry.

Isoindigo is highly regarded as an electron Acceptor(A) component of organic D-A semiconductors. It can be prepared as follows:

Scheme 1: This is but one route to the isoindigos(see refs. for others); however it is another illustration of the importance of lactam derivatives in organic semiconductor technology(OSC).


The following are additional procedures with chemistry related to my proposals:
Isotin readily reacts with oxindole to form isoindigos by Knoevenagel condensation. My proposal is to place these difunctionalities on the same or separate compounds so that their condensation will form a polymer.

Thinking about this chemistry, I have several proposals:
Scheme 2: This would be a type of “polyisoindigo” actually a benzodipyrroledione. The MW can be controlled by the addition of isoindigo. Such capping monomers can be derivatized with bromines. For example:

Scheme 3: Oxindole and or isotin could be added to the reaction mixture to limit the MW. Alternatively an excess of either difunctional monomer(E or F) would determine which capping monomer should be used. These oligomers/polymers, I believe, would be super Acceptors and with suitable Donors (attached by coupling reactions through the bromines) would produce very active organic semiconductors. I do not believe the MW of said polymers would be very high most likely they would be oligomers because the literature indicates moderate yields for these reactions. Even if n=2, the possibility of unexpected properties might be expected.
Obviously many aromatic donor combinations can be employed to couple with said oligomers/polymers and they are reviewed in several recent articles.


Kelly et. al. demonstrate that the position of the coupling bromine on the isoindigo benzene ring is very important to performance. For example:

![Scheme 3](image)


They show that coupling to the 6,6 positions results in the best performing OSC's. Obviously the bromines are in the wrong position and should have been at the 6,6' position in scheme 3 to afford the more potent quinoidal structure possibility.

![Scheme 4](image)

Scheme 4: Monomers A & B (benzodifurandione) can also take part in this type of condensation polymerization. They can be mixed in as comonomers with E & F from scheme 2 for example.


References to similar polymers to the above have recently been published; for example the following monomers were polymerized:

**Pyrazine derivative polymers**

Scheme 5: A review of the synthesis of the alpha-amino ketone starting compounds are covered in my previous proposals for DPP and isoDPP pdfs (see my web page). See scheme 2 for an example of the bis-oxindole comonomer that would be the other component required for polymerization. Alternatively, scheme 5 monomer can be converted into another type of polymer:

Scheme 6: The polymer would probably be very insoluble and therefore, the benzenes would have to be derivatized with typical solubilizing R groups.


**Additional synthesis ideas (Knoevenagel condensation):**
Scheme 7: The isotin benzene ring can have a 6-bromine substitution suitable for coupling of donor moieties.

A structure search in SciFinder revealed no references for unsaturated bis-lactam A; therefore, I want to propose two possible syntheses:

Scheme 7: The possibility that the proposed position of the unsaturation in G would alternatively conjugate with one of the carbonyls might be a problem? I'm sure there must be other possible synthesis routes, for example; another approach is to oxidize the saturated bis-lactam after the synthesis:
Scheme 8: Although other stereochemistry is possible, the Z,Z orientation of the diene is well known and depends on the hydrogenation catalyst.


If oxidation will produce the required unsaturation, then the following would be possible:

Scheme 9: This polymeric acceptor would be a very active OSC intermediate component that could be capped with isoindigos and coupled to Donor components after condensation to the 6- bromine substituted isoindigo.

Oxidation does work for DPP precursors, but would probably require experimental development to also work for those in scheme 9:

Scheme 8. Synthesis of DPP by the oxidation of compound 11.
“Similarly to nitriles, Schiff bases condense with succinic acid esters. The products are compounds of type 11, i.e., derivatives of hexahydropyrrolo[4,3-c]pyrrole-1,4-dione, which can be considered a saturated analogue of N,N-diaryl DPP (Scheme 8). Chemists from Ciba-Geigy found that compound 11 can be oxidized to the corresponding DPP using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) as an oxidant (Scheme 8).”


Thank you for reading these proposals.

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