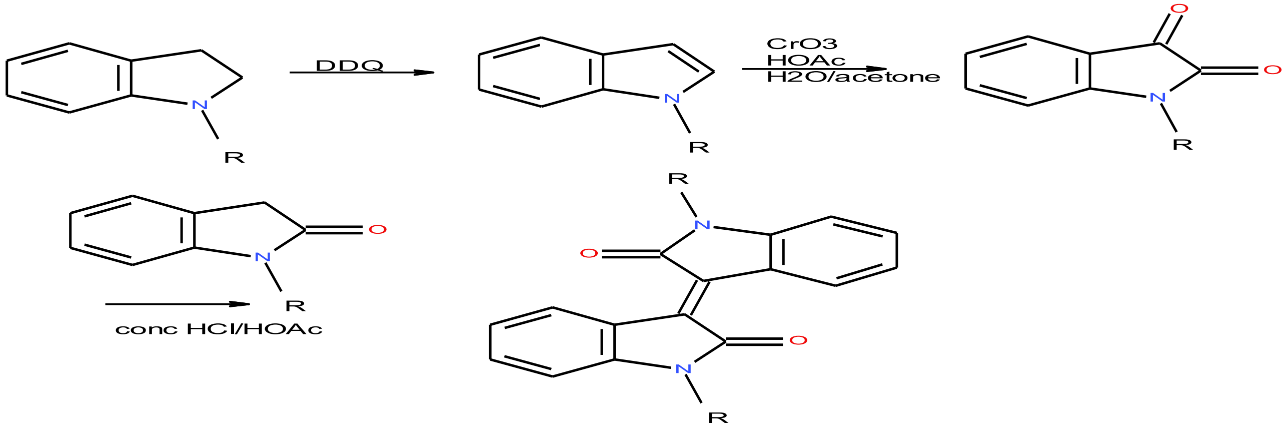
Polymeric Isoindigo, benzodifurandione and benzodipyrrolediones

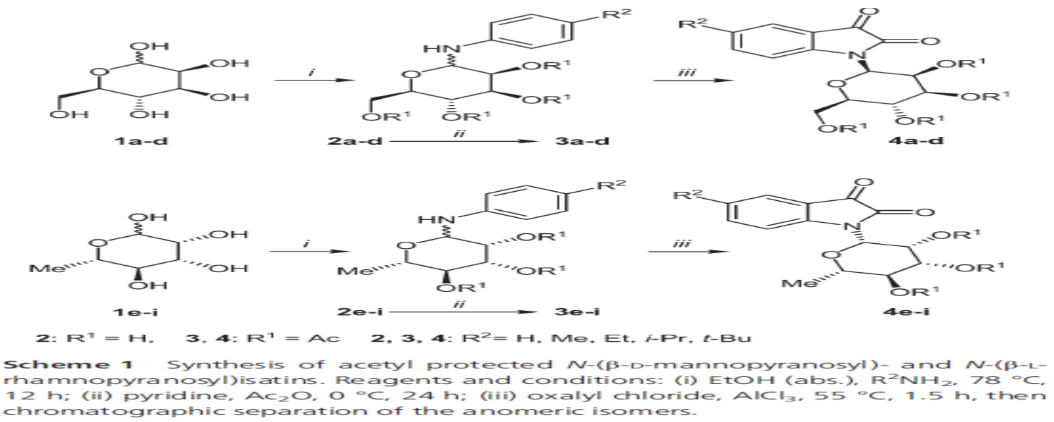
by; Robert B. Login http://rloginconsulting.com/joomla/

With the 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).



2: R^1 = H, **3**, **4**: R^1 = Ac **2**, **3**, **4**: R^2 = H, Me, Et, *i*-Pr, *t*-Bu

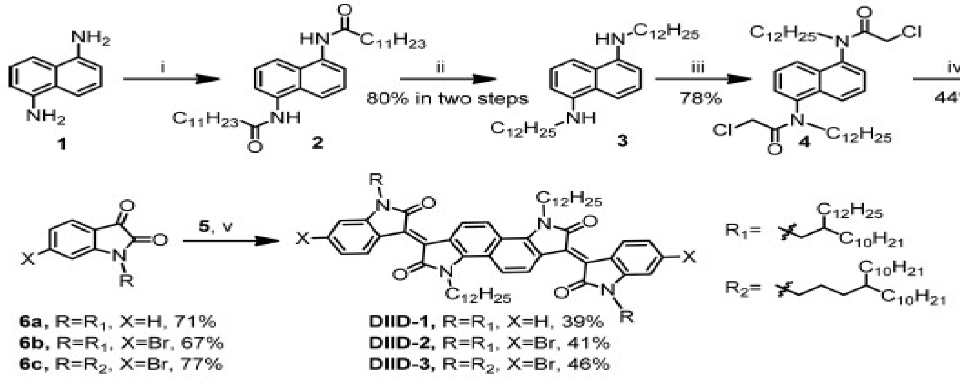
Scheme 1 Synthesis of acetyl protected *N*-(β-D-mannopyranosyl)- and *N*-(β-L-rhamnopyranosyl)isatins. Reagents and conditions: (i) EtOH (abs.), R^2NH_2, 78 °C, 12 h; (ii) pyridine, Ac_2O, 0 °C, 24 h; (iii) oxalyl chloride, $AlCl_3$, 55 °C, 1.5 h, then chromatographic separation of the anomeric isomers.

Kleeblatt, Dennis, et al. "Synthesis of N, N′-diglycosylated isoindigos."*Organic & biomolecular chemistry",* 11.6 (2013): 886-895.

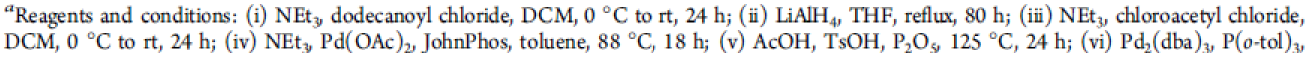
Da Silva, Joaquim FM, Simon J. Garden, and Angelo C. Pinto. "The chemistry of isatins: a review from 1975 to 1999."*Journal of the Brazilian Chemical Society",* 12.3 (2001): 273-324.

Bogdanov, Andrei V., Lenar I. Musin, and Vladimir F. Mironov. "Advances in the synthesis and application of isoindigo derivatives."*ARKIVOC: Online Journal of Organic Chemistry",* 2015 (2015).

The following are additional procedures with chemistry related to my proposals:

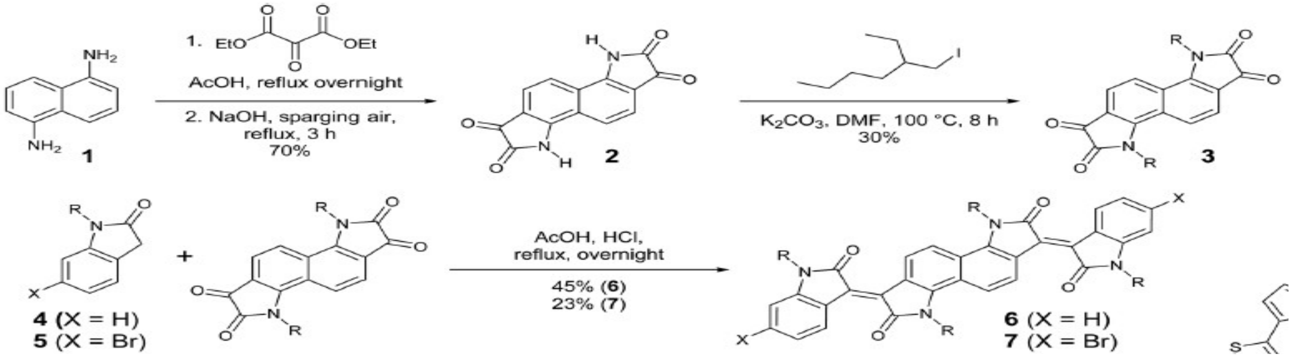


Jiang, Yu, et al. "Synthesis and Characterization of Isoindigo [7, 6-g] isoindigo-Based Donor–Acceptor Conjugated



[a]Reagents and conditions: (i) NEt_3, dodecanoyl chloride, DCM, 0 °C to rt, 24 h; (ii) $LiAlH_4$, THF, reflux, 80 h; (iii) NEt_3, chloroacetyl chloride, DCM, 0 °C to rt, 24 h; (iv) NEt_3, $Pd(OAc)_2$, JohnPhos, toluene, 88 °C, 18 h; (v) AcOH, TsOH, P_2O_5, 125 °C, 24 h; (vi) $Pd_2(dba)_3$, $P(o\text{-tol})_3$,

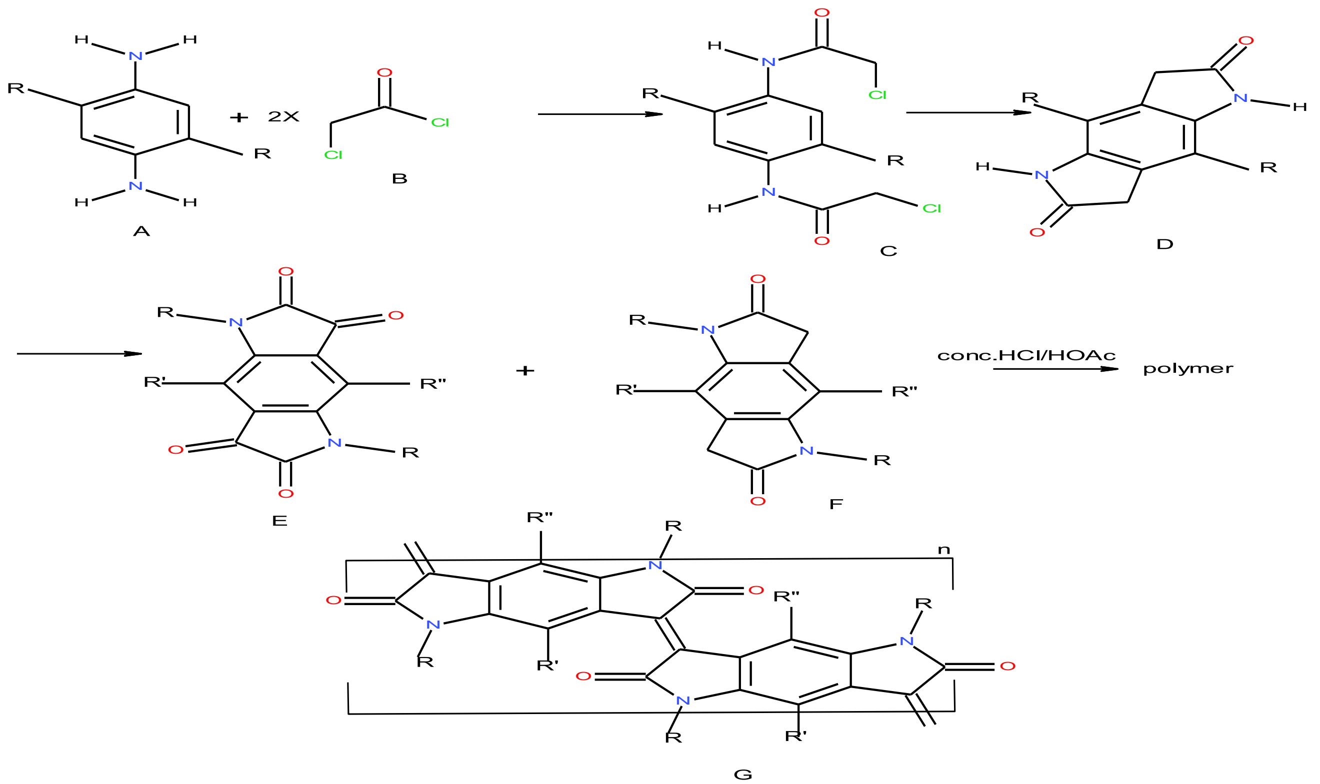
Polymers."*Macromolecules",* 49.6 (2016): 2135-2144.



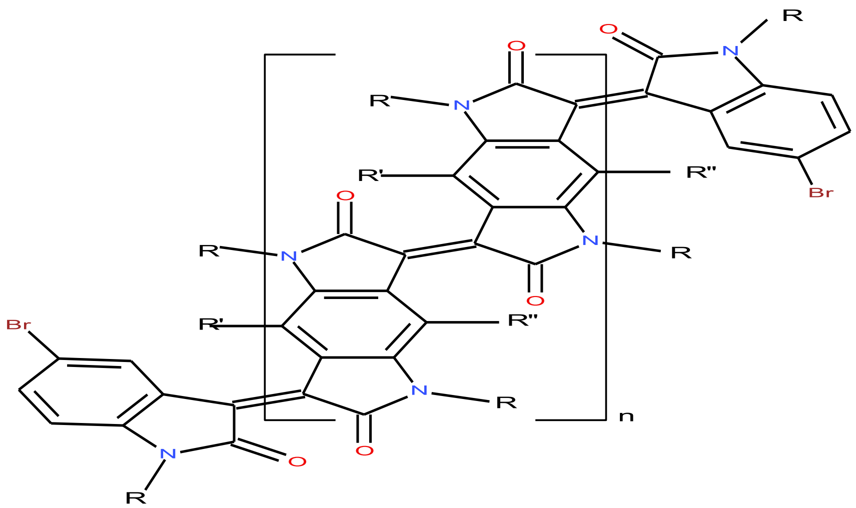
Randell, Nicholas M., Philip C. Boutin, and Timothy L. Kelly. "Bisisoindigo: using a ring-fusion approach to extend the conjugation length of isoindigo."*Journal of Materials Chemistry A",* 4.18 (2016): 6940-6945.

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.

Quinn, Jesse TE, et al. "Recent progress in the development of n-type organic semiconductors for organic field effect transistors."*Journal of Materials Chemistry C",* 5.34 (2017): 8654-8681.

Shi, Longxian, et al. "Design and effective synthesis methods for high-performance polymer semiconductors in organic field-effect transistors."*Materials Chemistry Frontiers",* 1.12 (2017): 2423-2456.

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

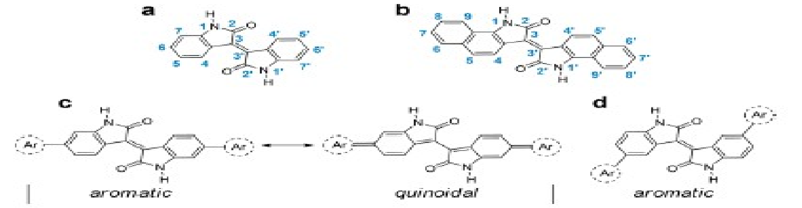
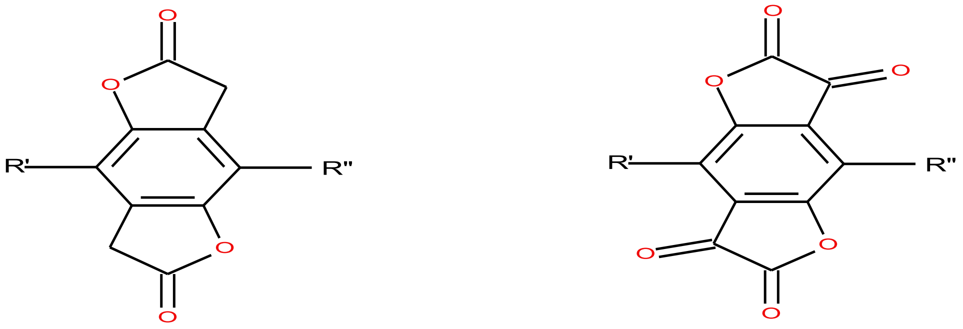


Figure 1. Structure and numbering scheme of (a) isoindigo and (b) benzoisoindigo; isoindigo-based D—A compounds with (c) a linearly conjugated 6,6′-linkage and (d) a cross-conjugated 5,5′-linkage.

Ganguly, Anindya, Jianfeng Zhu, and Timothy L. Kelly. "Effect of Cross-Conjugation on Derivatives of Benzoisoindigo, an Isoindigo Analogue with an Extended π-system."*The Journal of Physical Chemistry C",* 121.17 (2017): 9110-9119.

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.



A

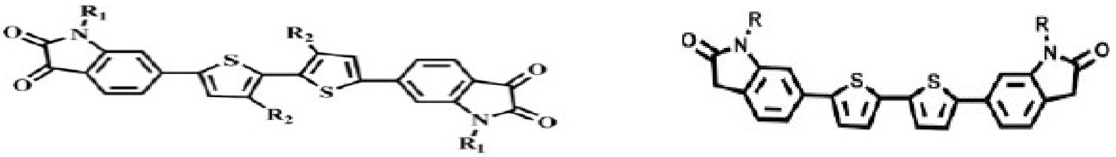
B

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.

Quinn, Jesse TE, et al. "Recent progress in the development of n-type organic semiconductors for organic field effect transistors."*Journal of Materials Chemistry C ",* 5.34 (2017): 8654-8681.

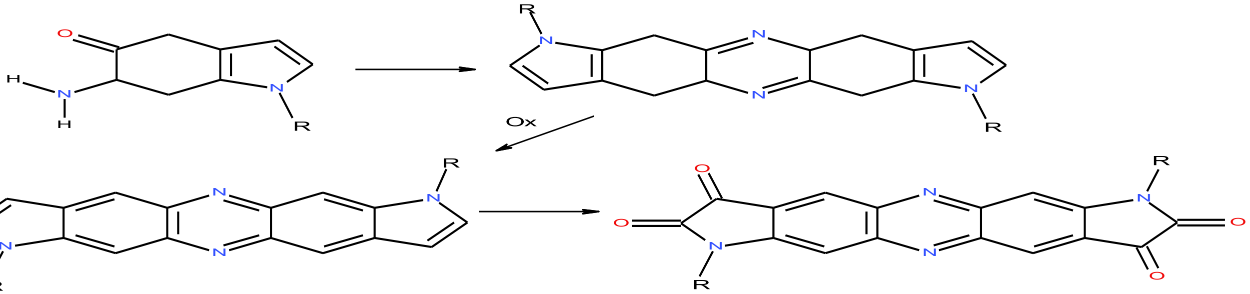
Jiang, Yu, et al. "Synthesis and Characterization of Isoindigo [7, 6-g] isoindigo-Based Donor–Acceptor Conjugated Polymers."*Macromolecules",* 49.6 (2016): 2135-2144.

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

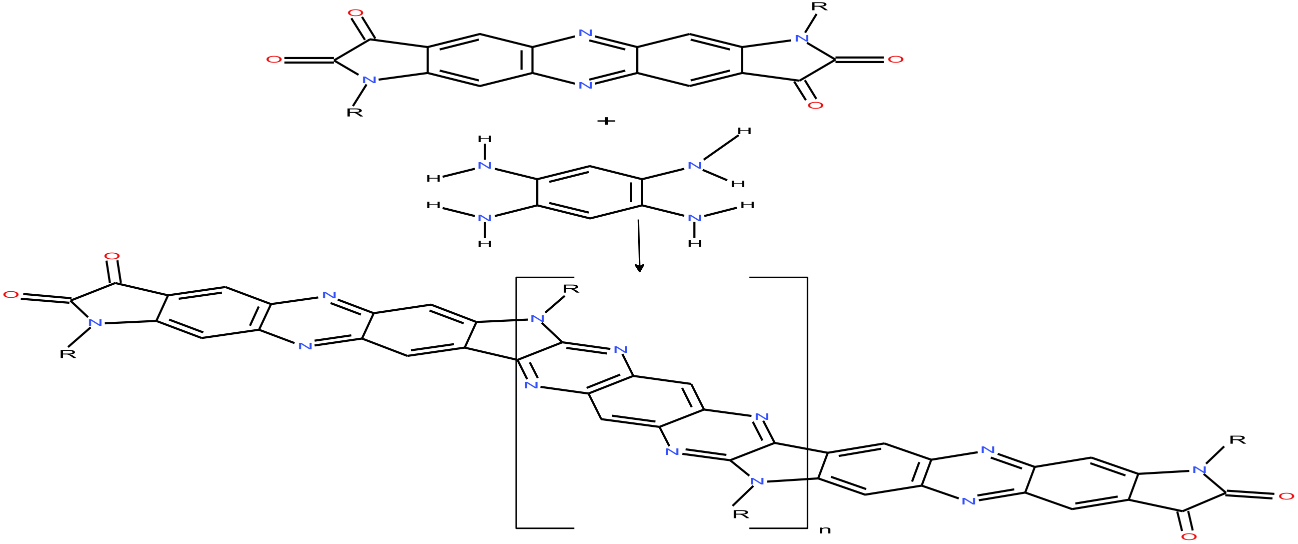


Zhang, Guobing, et al. "Facile green synthesis of isoindigo-based conjugated polymers using aldol polycondensation."*Polymer Chemistry",* 8.22 (2017): 3448-3456.

Pyrazine derivative polymers



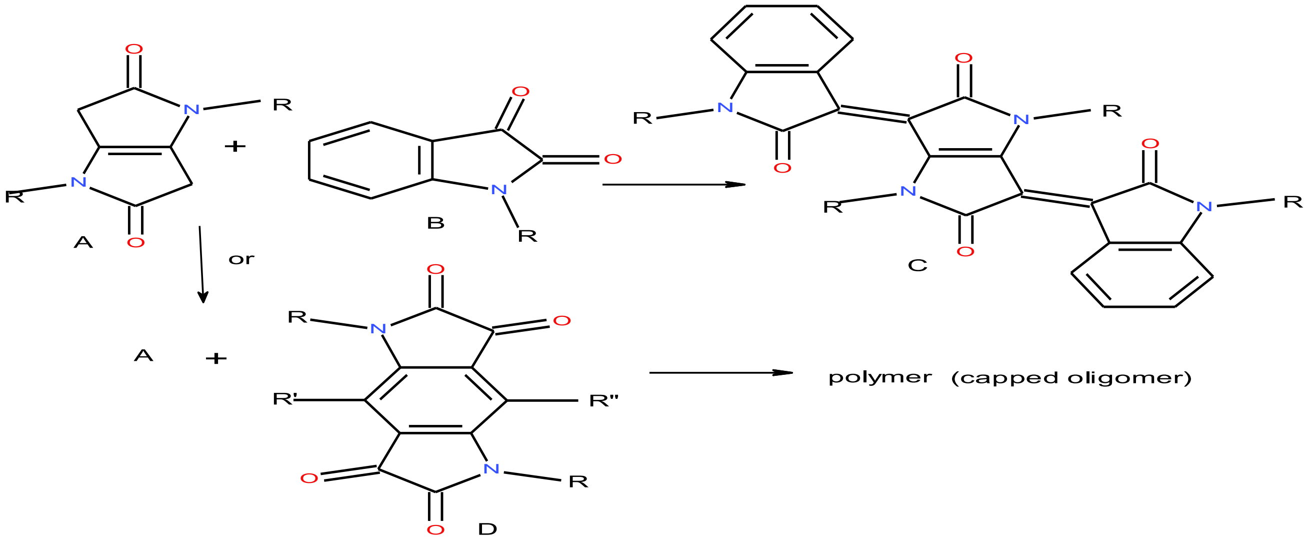
Scheme 5: A review of the synthesis of the alpha-amino ketone starting compounds are covered in my previous proposals for DPP and isoDPP pdfs(see my web page). See scheme 2 for an example of the bis-oxindole comonomer that would be the other component required for polymerization. Alternatively, scheme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

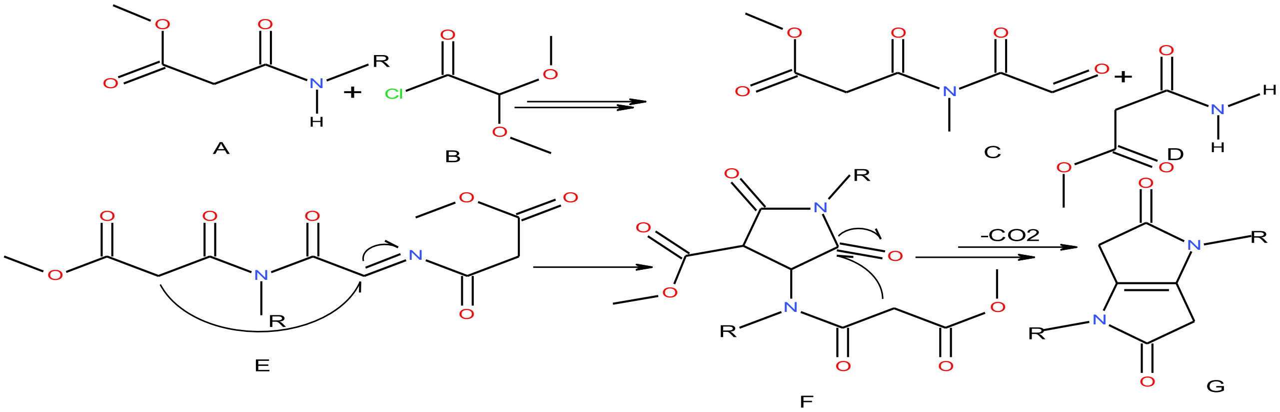
Driller, Katrin Marie, et al. "Synthesis of 6 H-indolo [2, 3-b] quinoxaline-N-glycosides and their cytotoxic activity against human ceratinocytes (HaCaT)."*Organic & biomolecular chemistry",* 6.22 (2008): 4218-4223.

Additional synthesis ideas(Knoevenagel condensation):

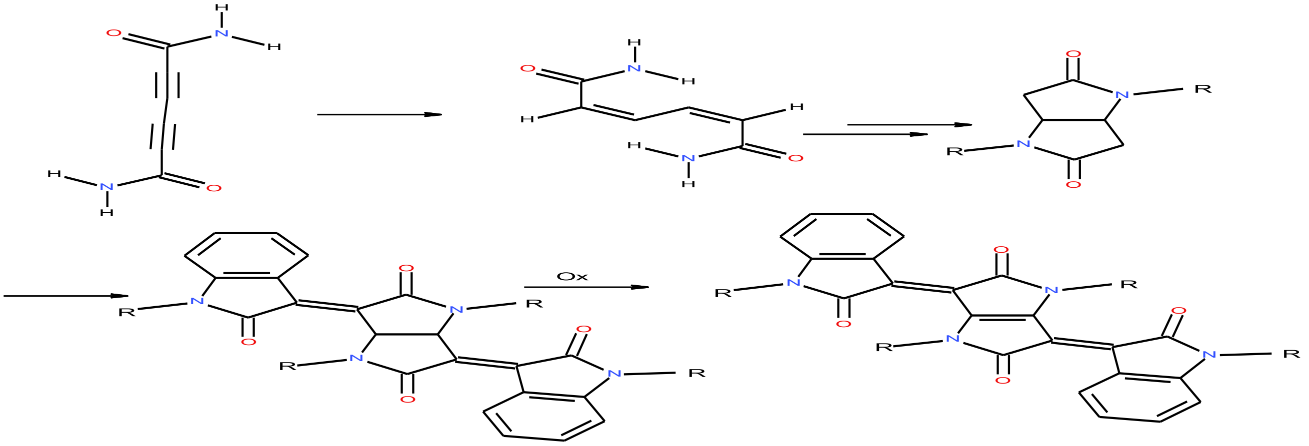


Scheme 7: The isotin benzene ring can have a 6-bromine substitution suitable for coupling of donor moieties.

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



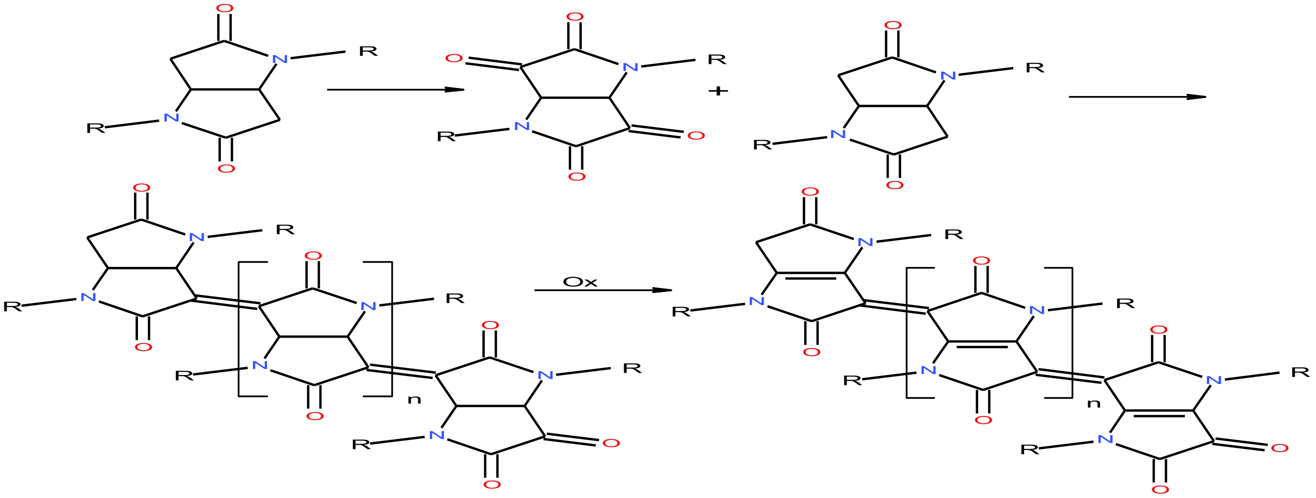
Scheme 7: The possibility that the proposed position of the unsaturation in G would alternatively conjugate with one of the carbonyls might be a problem? I'm sure there must be other possible synthesis routes, for example; another approach is to oxidize the saturated bis-lactam after the synthesis:



Scheme 8: Although other stereochemistry is possible, the Z,Z orientation of the diene is well known and depends on the hydrogenation catalyst.

Thiel, Niklas O., Sebastian Kemper, and Johannes F. Teichert. "Copper (I)-catalyzed stereoselective hydrogenation of 1, 3-diynes and enynes."*Tetrahedron",* (2017).

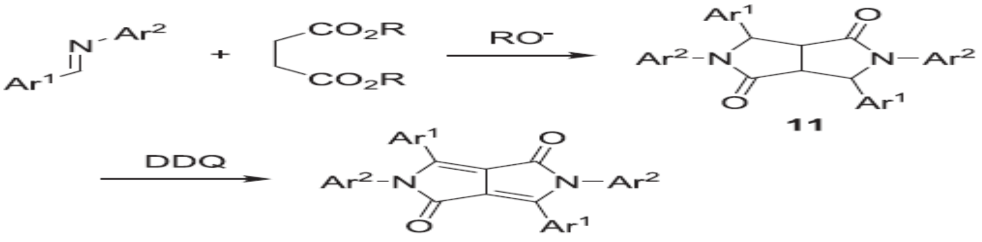
If oxidation will produce the required unsaturation, then the following would be



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**). [15] Chemists from Ciba-Geigy found that compound **11** can be oxidized to the corresponding DPP using 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) as an oxidant (Scheme 8).”

Grzybowski, Marek, and Daniel T. Gryko. "Diketopyrrolopyrroles: Synthesis, reactivity, and optical properties."*Advanced Optical Materials”,* 3.3 (2015): 280-320.

Thank you for reading these proposals.

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