Pechmann Dye Homopolymers

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Organic semiconductors compounds continues to fascinate me. Especially those related to the pyrrolidone type derivatives. It just strikes me as amazing that this lactam moiety can play such an important part in such compounds. With this in mind, Pechmann dyes can be both lactone and lactam derivatives with several unusual semiconductor properties. A review of their synthesis is where I will begin.

"It has now been found that the yields of the original process can be raised to 80% and above by the simple expedient of adding cuprous chloride and ammonium chloride to the reaction mixture of benzoylacrylic acid (IIa) and acetic anhydride. In addition to the preparation of Pechmann's dye this method has been used for the synthesis of the p,p-diphenyl derivative (\-Id) and the new di-(m-nitro) derivative (We) in yields of 80% and 73% respectively."

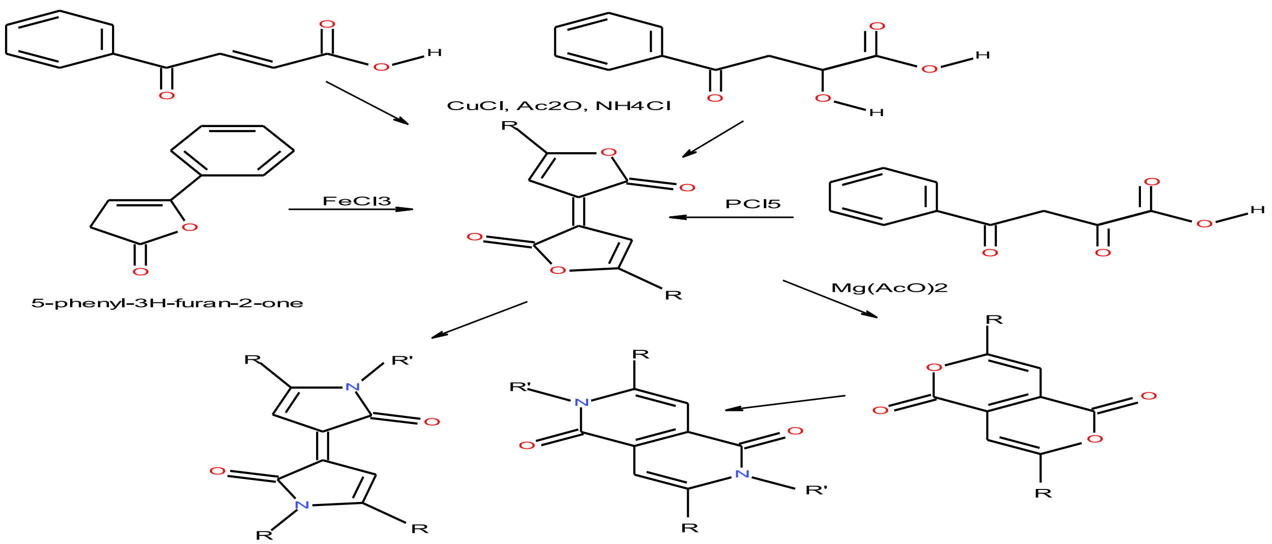
Fang, Chen Shang, and Werner Bergmann. "Pechmann's Dye and Related Compounds."*The Journal of Organic Chemistry"* 16.8 (1951): 1231-1237.

USP 2,640,836 Bergmann, Werner. "Process for producing Pechmann dye." (1953).

USP 2,640,837 James, Chen-Shang Fang, and Werner Bergmann. "Process for the preparation of Pechmann dye." (1953).

"The compounds can be prepared by several methods e.g. dehydration of beta -aroylacrylic acids with acetic anhydride, oxidation of 3 -phenylbutenolactones with ferric chloride, self condensation of ethyl benzoylpyruvate with phosphorus pentachloride and condensation of 3 -keto and 3 -diketoacids. A slight modification of the first method by addition of cuprous chloride and ammonium chloride allows a large increase in yield of the compound (Fang and Bergmann, 1951)."

RAHMANI, MAWARDI, and LESLIE CROMBIE. "5, 5'-Diarylbifuranylidenediones and their 6, 6-Dilactone Isomerisation Products."Center *for Extension and Continuing Education"*: 81.



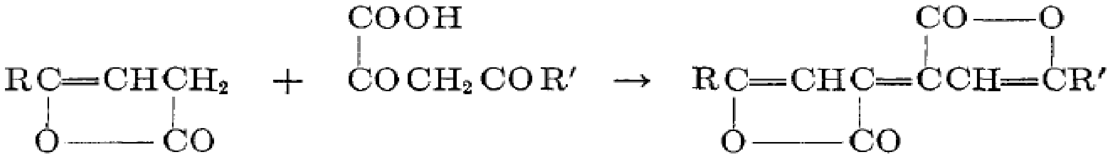
Scheme 1: Summary of pathways to Pechmann dyes. There is a patent that illustrates another method:

Sauer, John C. "Dilactones and their preparation from carbon monoxide and acetylenes." U.S. Patent No. 2,840,570. 24 Jun. 1958.

Another approach revolves around a double Morita-Bayliss type reaction of dimethyl maleate.

Hopf, Henning, et al. "A Facile Synthesis of Pechmann Dyes."*Chemistry-A European Journal",* 20.19 (2014): 5565-5568. For example:

"Synthesis of bislactone 2; General Procedure
To a solution of *N*-phenacyl-4-dimethylaminopyridinium bromide (**1**, 1 g, 3.1 mmol) in dioxane (30 mL) a solution of DBU (0.81 mL, 6.2 mmol) in dioxane (2 mL) was added at rt. Dimethyl maleate (0.95 mL, 6.2 mmol) was then added and the reaction mixture was heated at 80 °C for 6 h. After cooling to rt the solvent was evaporated under vacuum and the residue was diluted with ethanol in order to separate bislactone **2**. This was filtered off and washed with ethanol to get compound **2** as a yellow fluorescent solid; M.p. 321-323 °C, Lit[1]: 317 °C; yield 0.38 g (40%)."



$$\underset{\mathrm{O}\text{———}\mathrm{CO}}{\mathrm{RC{=}CHCH_2}} + \overset{\mathrm{COOH}}{\mathrm{COCH_2COR'}} \rightarrow \underset{\mathrm{O}\text{———}\mathrm{CO}}{\mathrm{RC{=}CHC}}\overset{\mathrm{CO{-}{-}O}}{\mathrm{{=}CCH{=}CR'}}$$

This general method has been used to prepare a number of symmetrically and unsymmetrically substituted dyes. In the latter case it has been shown that identical products are obtained when R and R′ are interchanged in the reactants; in other words, that the chromophore of the Pechmann dye is symmetrical (7, 13).

Klingsberg, Erwin. "The Chemistry of the Pechmann Dyes."*Chemical Reviews",* 54.1 (1954): 59-77.

Overview of possibilities:

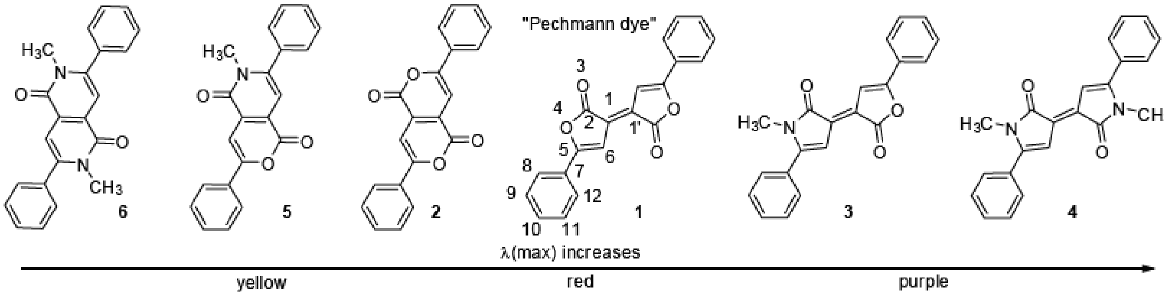


Fig. 1. Pehcmann dye (**1**), ring-rearranged (**2**), N-methylamidated (**3**,**4**) and ring rearranged, N-methylamidated derivatives (**5**,**6**).

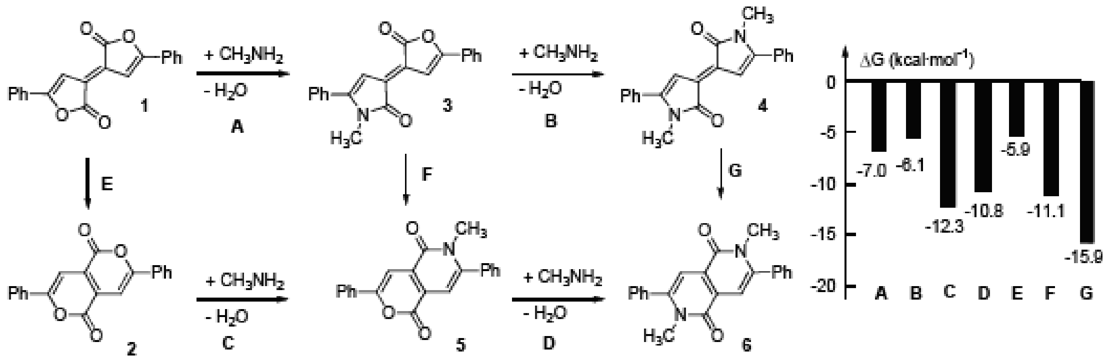
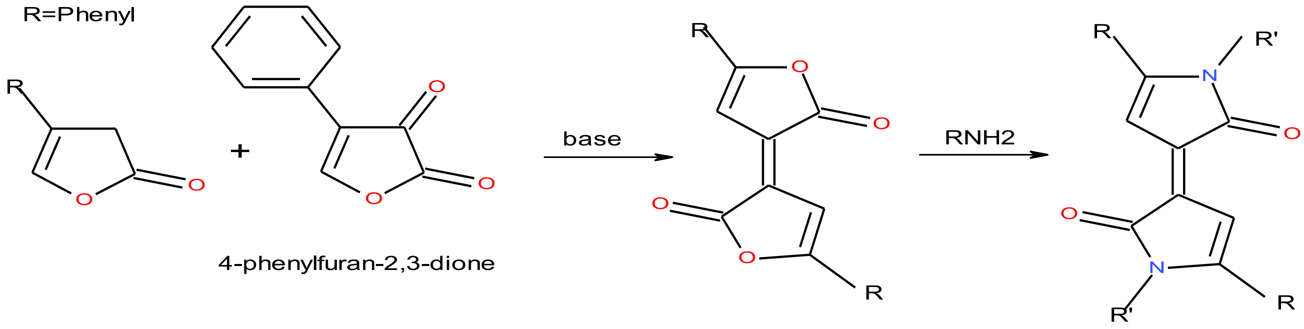


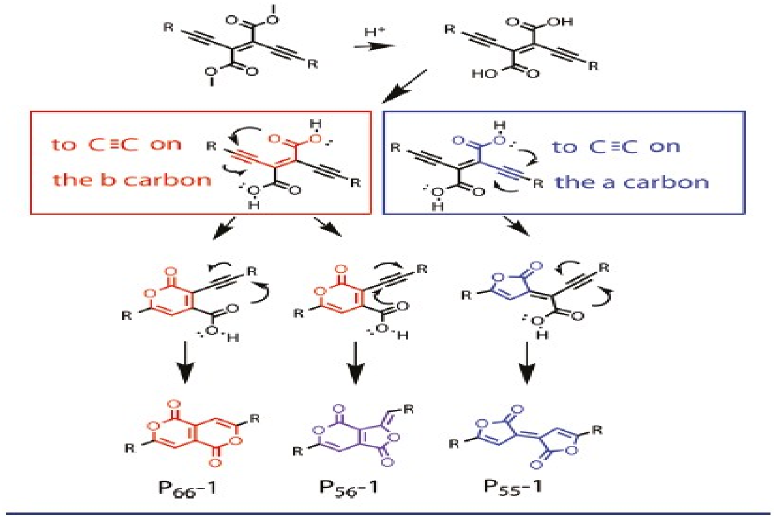
Fig. 3. Evaluation of ΔG (SCRF=SMD, $CHCl_3$/B3LYP/DGDZVP) for the conversion of the Pechmann dye (**1**) into the core heterocycle-rearranged, amidated and heterocycle rearranged, amidated derivatives.

Kantchev, Eric Assen B., Tyler B. Norsten, and Michael B. Sullivan. "Chemically accurate and computationally-efficient time-dependent density functional theory (TDDFT) modeling of the UV/Vis spectra of Pechmann dyes and related compounds."*Procedia Computer Science",* 4 (2011): 1157-1166.

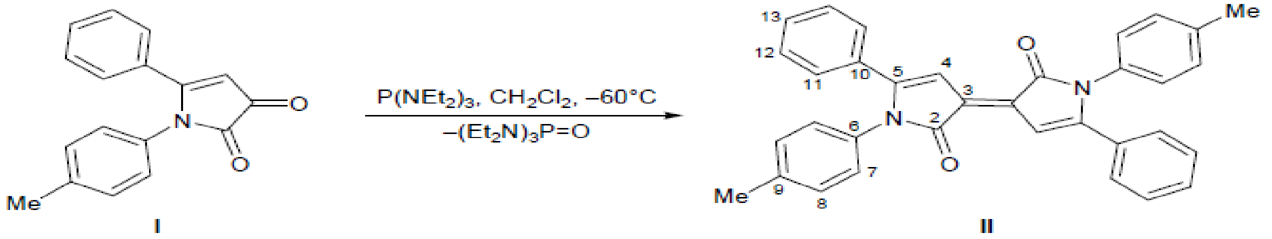


Scheme 2: Similar example in Flores, Jean-Charles, et al. "Ketopyrroles as organic semiconductors." U.S. Patent No. 8,758,880. 24 Jun. 2014.

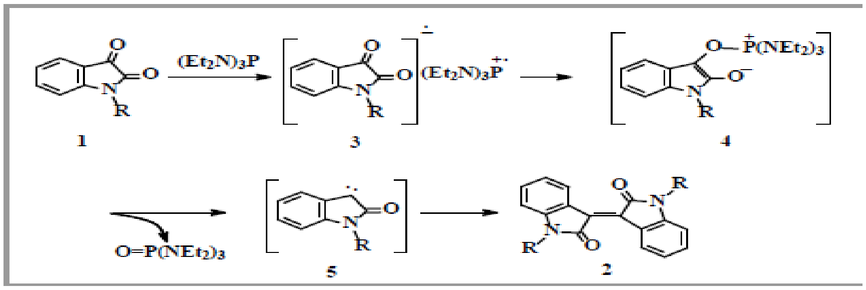
Scheme 3. Plausible Reaction Mechanism of Double Lactonization in *E*-1 (R = Triarylamino Group)



Hayashi, Mikihiro, et al. "Double lactonization in triarylamine-conjugated dimethyl diethynylfumarate: formation of intensely colored and luminescent quadrupolar molecules including a missing structural isomer of pechmann dyes."*Journal of the American Chemical Society",* 133.37 (2011): 14518-14521.



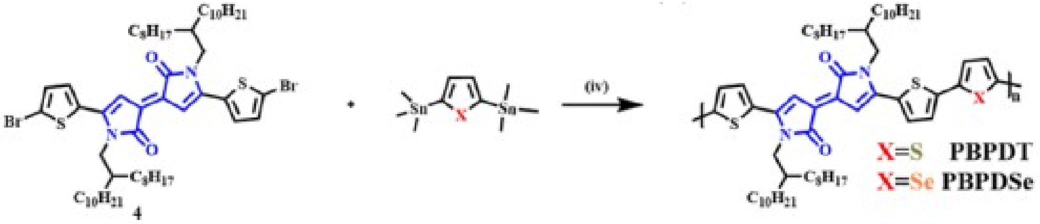
Musin, L. I., A. V. Bogdanov, and V. F. Mironov. "Reaction of 1-(4-methylphenyl)-5-phenyl-2, 3-dihydro-1H-pyrrole-2, 3-dione with tris (diethylamino) phosphine. A new synthesis of 3, 3′-bipyrrolylidene-2, 2′-dione derivatives."*Russian Journal of Organic Chemistry”,* 50.7 (2014): 1058-1059.



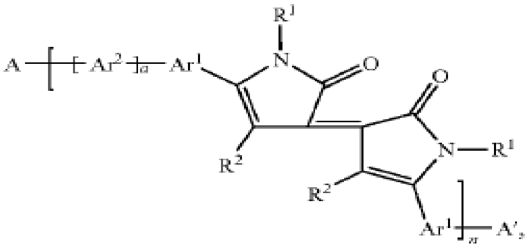
Scheme 2 Proposed mechanism for the reaction

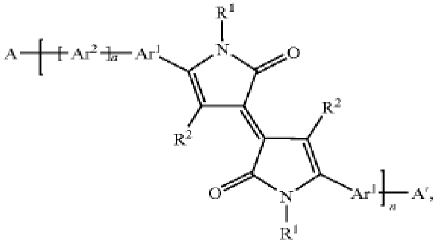
Bogdanov, Andrei V., et al. "Facile synthesis of 1, 1′-dialkylisoindigos through deoxygenation reaction of isatins and tris (diethylamino) phosphine."*Synthesis”,* 2010.19 (2010): 3268-3270.

Many polymeric derivatives of Pechmann dyes are known but all that I found are based on coupling reactions. The dyes are very electron deficient and are coupled to electron rich monomers or oligomers. For example:



Yang, Si-Fen, et al. "Conjugated Donor–Acceptor Polymers Entailing Pechmann Dye-Derived Acceptor with Siloxane-Terminated Side Chains Exhibiting Balanced Ambipolar Semiconducting Behavior."*Macromolecules”,*49.16 (2016): 5857-5865.





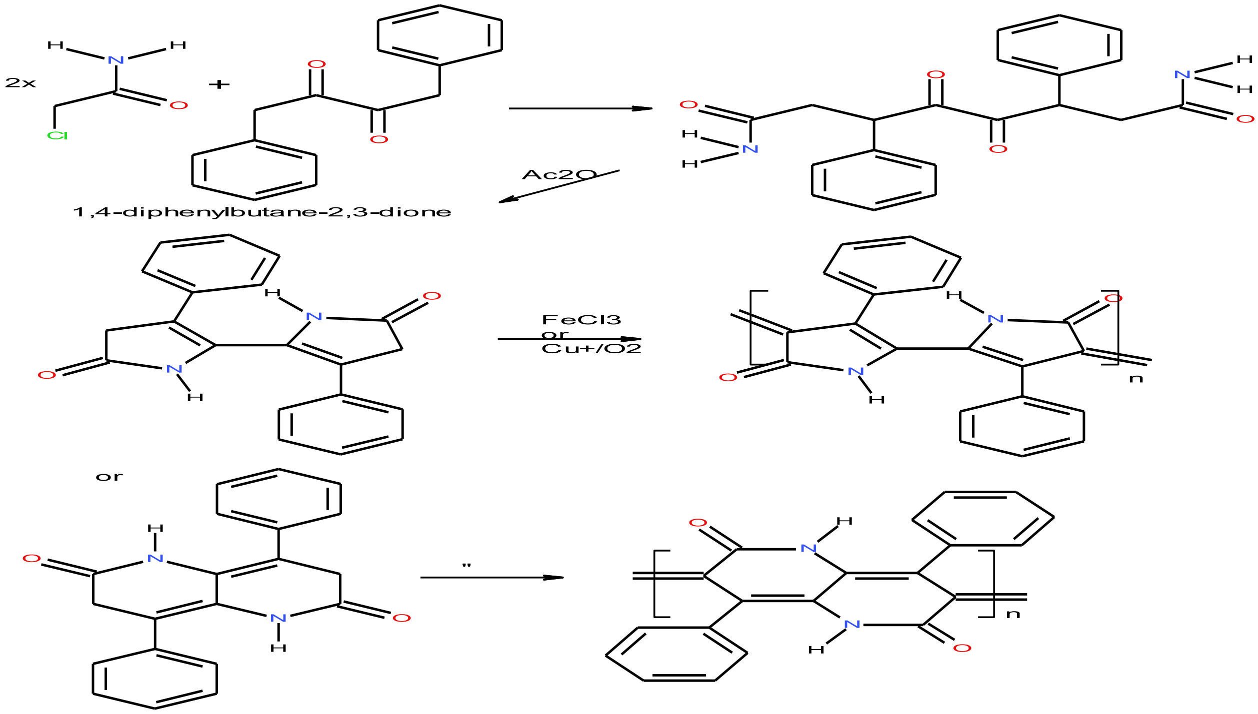
Flores, Jean-Charles, et al. "Ketopyrroles as organic semiconductors." U.S. Patent No. 8,758,880. 24 Jun. 2014.

This patent illustrates that these dyes can be both cis and trans(preferred) and the polymeric general examples are D-A, D-A-D or A-D-A or various combinations. This is done to increase the spectrum that these combinations can capture photons which results in much better PCE (power conversion efficiency).

Very recently a paper has appeared that illustrates the benefits of A type homopolymers. “Donor–acceptor (D–A) type conjugated polymers have been extensively studied for organic field-effect transistors (OFETs), while the homopolymers of acceptors were much less investigated. However, conjugated homopolymers are structurally simpler, so their solid-phase behavior such as packing pattern, long-range order and crystallinity are more predictable, so are their charge-transport properties.”

Zhang, Huanrui, et al. "One-pot homopolymerization of thiophene-fused isoindigo for ambient-stable ambipolar organic field-effect transistors."*RSC Advances”,*7.40 (2017): 25009-25018.

This ends my review of the synthesis of Pechmann dyes. I will now present my proposal. For example:

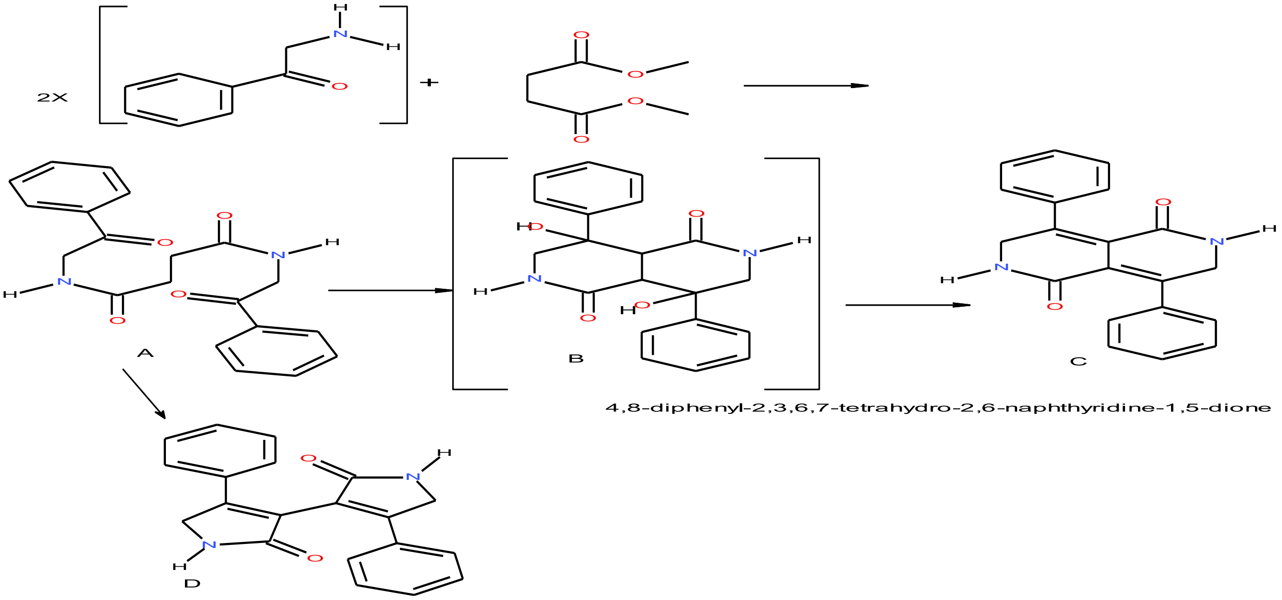


Scheme 3: Pechmann dye homopolymer proposal. Notice that five and six membered rings or mixtures would seem possible. Also the amide probably will have to be protected with an R group before FeCl3 condensation? Alternatively 2-bromoacetyl esters can be used to form the butenolide which can then be post converted to the lactam. See the following reference for similar examples;

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

If you take a look at my previous pdf on a related chemistry, DPP analogs based on

Alpha-Amino Ketones , you will see that the monomers and polymers of scheme 3 are isomers of those prepared from alpha-amino ketones. They are “iso DPP's”. Applying Pechmann chemistry, especially where said monomers can be polymerized with oxidants such as FeCl3, is not possible with these DPP monomers because the ring methylenes are not alpha to the carbonyls. For example:



Scheme 4: Alpha-amino Ketone generated DPP types for comparison.

Thank you for reading my proposals. Questions or corrections are welcomed.
Dr. Robert B. Login http://rloginconsulting.com/joomla/