Indane-1,3-dione Based Vinyl and Alkyne and Singlet-Fission based Polymers

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This is a continuation of my interest in indane-1,3-dione polymeric derivatives. Please look at my previous article "Polymeric Organic Solar Cells " on my web page.

In the interim I have become fascinated with Singlet Fission which is the ability of organic materials to produce two lower energy triplet exitons from one high energy photon. This suggests that an acceptor such as a PDI type, if properly designed, could react with high energy photons, to contribute additional exitons that can be converted to free electrons and holes instead of just separating CTS and being a conduit for electron transfer. It is known that acceptors can capture photons and also contribute to the solar cell by chanel 2.
What I want to propose is structures that could be both acceptors and SF generators.

My proposal is to accomplish this idea with vinyl and/or alkyne polymerization. Before I propose SF ideas, I want to first propose unique indandione monomers.

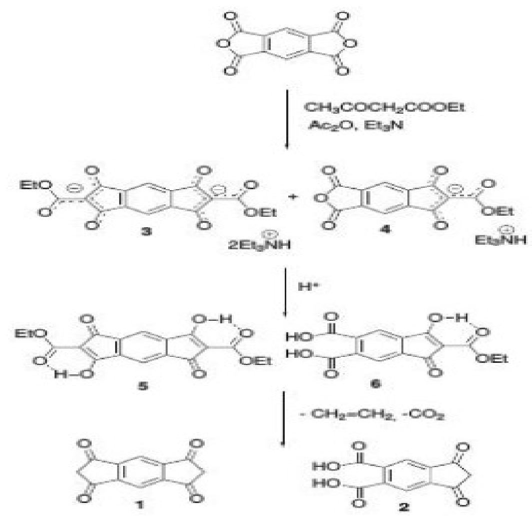
Vinyl 1,3-Indanone:

The synthesis of vinyl indane-1,3-dione can be accomplished starting from phthalic anhydride. 5-Ethenyl-2-benzofuran-1,3-dione

"The synthesis of 4-vinyl-1, 2-phthalate esters via Suzuki coupling"
Braslau, R., Schäffner, F., & Earla, A. (2013). Polymeric phthalates: Potential nonmigratory macromolecular plasticizers. *Journal of Polymer Science Part A: Polymer Chemistry*, *51*(5), 1175-1184.

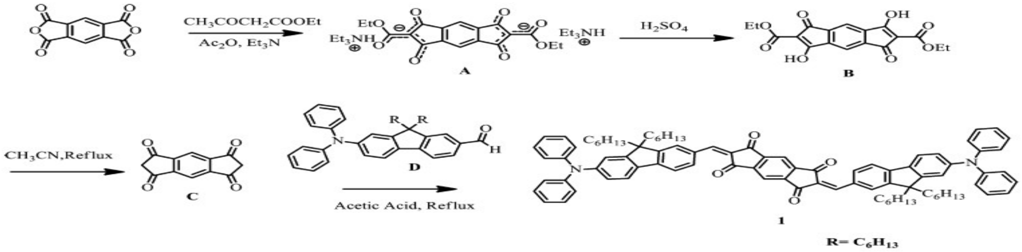
The Diels-Alder reaction between 2-ethyl butadiene and dichloromaleic anhydride led to the formation of 4-ethyl phthalic anhydride which was esterified, α-brominated in the side chain by NBS, and dehydro-brominated by heat.
Tahan, M., Perez, D., & Zilkha, A. (1971). Synthesis of Some Polymeric Dyes. *Israel Journal of Chemistry*, *9*(2), 191-200.

Synthesis of Indane-1,3-diones from "phthalic anhydrides":



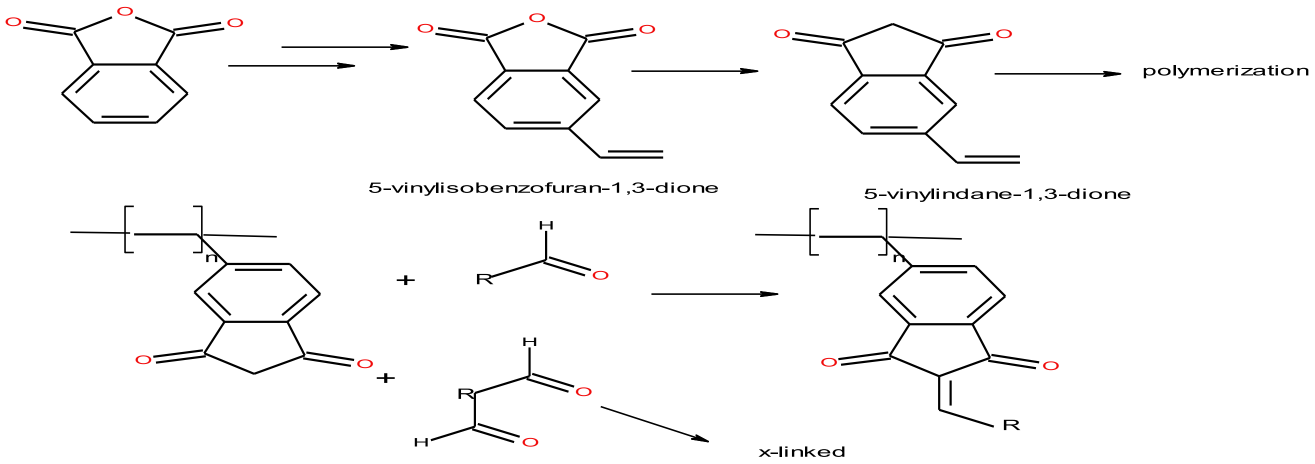
Krief, P., Becker, J. Y., Ellern, A., Khodorkovsky, V., Neilands, O., & Shapiro, L. (2004). s-Indacene-1, 3, 5, 7 (2H, 6H)-tetraone (‘Janus dione’) and 1, 3-Dioxo-5, 6-indanedicarboxylic acid: Old and New 1, 3-Indandione Derivatives. *Synthesis*, *2004*(15), 2509-2512.

Scheme 1. Synthesis of 1

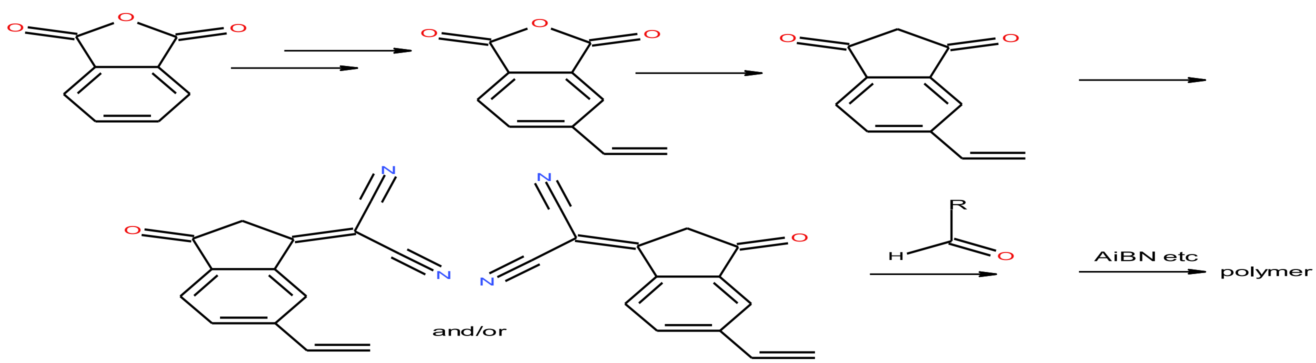


Githaiga, G. W., Woodward, A. W., Morales, A. R., Bondar, M. V., & Belfield, K. D. (2015). Photo physical and Computational Analysis of a Symmetrical Fluorene-Based Janus Dione Derivative. *The Journal of Physical Chemistry C*, *119*(36), 21053-21059.

(See my pdf “Polymeric Organic Solar Cells” on my web page for more examples.)

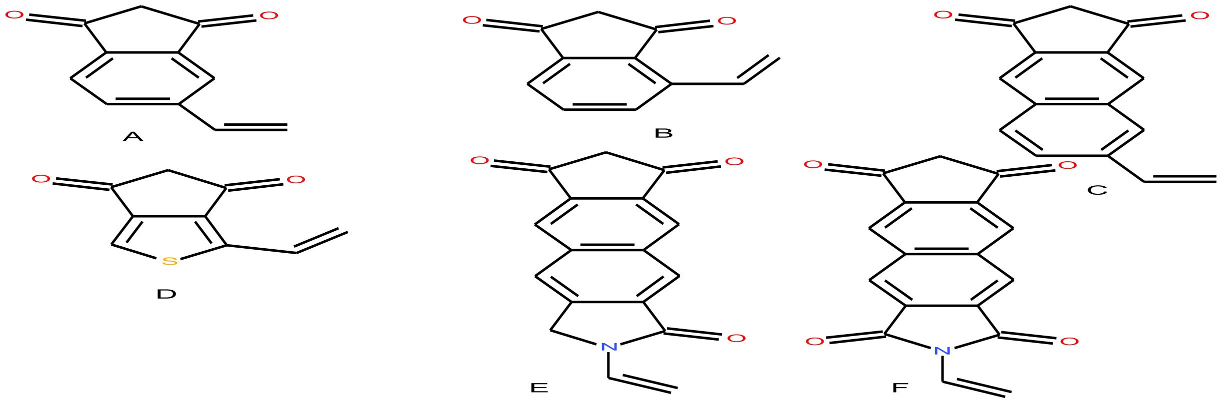


Scheme 1: The R group could be part of the dialdehyde compounds associated with organic solar cell acceptor synthesis.



Scheme 2: Functionalized monomer. This scheme illustrates the formation of the dicyanoethylene at the unpolymerized monomer stage. I would worry that this derivative would also participate in free radical polymerization. If so then it could conceivably be prepared post polymerization; although purification of the derivatised monomer would be advantages. I illustrate this monomer because it is related to the NFA's employed in OPV's.

If difunctional aldehydes used for acceptor synthesis are reacted with said polymers then crosslinked polymers, possibly gels would result. I don't think anyone has looked at the OPV properties of such gels? Gelation could be carried out in the presence of polymeric donors.



Scheme 3: Examples of vinyl monomers. Obviously many other polymerizable monomers of this type could be conceived of.

Copolymers with for example n-vinylpyrrolidone would be water soluble depending on the amount of 1, 3-Indandione derivative (such as A above) incorporated in the copolymer. Said water soluble copolymer could then be crosslinked with suitable dialdehydes to afford gels. Homopolymers of A for example could be crosslinked with compounds that would render the resulting crosslinked polymer a gel in aqueous solution.

Assuming that these monomers will polymerize by free radical initiation, would result in a wide variety of possible copolymers. They could be derivatized with the donor aldehyde intermediates resulting in poly-NFA's. I think this would afford interesting polymeric acceptors for use in organic photovoltaics.

Should these indandione monomers be condensed with both acceptor and donor aldehyde derivatives; then single polymer OPV's would be worth considering.

5-ethynylindane-1,3-dione:

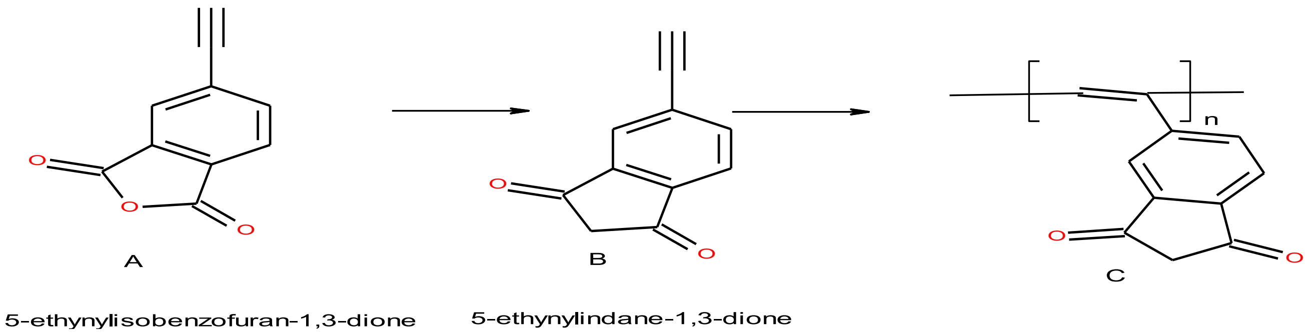
It is possible to brominate the 4 position of phthalic anhydride:

Wolk, J. L., & Frimer, A. A. (2010). A Simple, Safe and Efficient Synthesis of Tyrian Purple (6, 6′-Dibromoindigo). *Molecules*, *15*(8), 5561-5580.
Wolk, J. L., & Frimer, A. A. (2010). Preparation of Tyrian purple (6, 6′-dibromoindigo): past and present. *Molecules*, *15*(8), 5473-5508.

Vainberg, O., & Shorr, L. M. (1991). Bis (4-halo-phthalic acid) quarter salt, process for their preparation and their use.

The next step word be to synthesize the 5-ethynylindane-1,3-dione by the above methods.

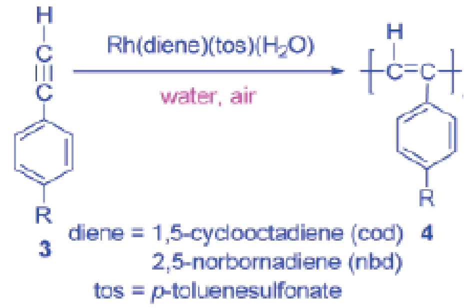
Acetylene polymerization would then be a possible.



Scheme 4: Alkyne based polymers and copolymers.

In this case polymer C can be crosslinked with acceptor dialdehyde intermediates. The difference here vs. vinyl indane-1,3-dione polymers is that the crosslinker is now conjugated with the unsaturated polymer backbone.

Lam, J. W., & Tang, B. Z. (2005). Functional polyacetylenes. *Accounts of chemical research*, *38*(9), 745-754.



Also:

Liu, J., Lam, J. W., & Tang, B. Z. (2009). Acetylenic polymers: syntheses, structures, and functions. *Chemical reviews*, *109*(11), 5799-5867.

Said conjugated polymers would be expected to be excellent conductors that would facilitate the transfer of holes and electrons. When derivatised with donors and acceptors, they should be self contained BHJ at the molecular level. With various dialdehyde donor and acceptor intermediates, ladder crosslinked gels would be synthetically possible.

Singlet Fission:

A recently published article spells out the current problems and possible remedies for the design of SF compounds.

Krishnapriya, K. C., Musser, A. J., & Patil, S. (2018). Molecular Design Strategies for Efficient Intramolecular Singlet Exciton Fission. *ACS Energy Letters*.

I must admit that I'm not a physicist and I'm concerned that I'm in deep water here but who else but an Organic/Polymer chemist might have ideas for interesting structures? As the above article points out, that much of the prior work to elucidate the mechanism of SF was done with polyaromatics that are unsuitable because of oxidative instability for OPV applications. They however have revealed the mechanism of SF which the following Yablonski diagram illustrates.

$S_0 + S_1 \rightleftarrows (TT) \rightleftarrows T_1 + T_1$

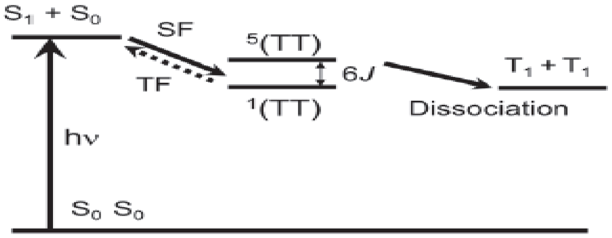


Fig. 1. Diagram of the singlet fission system. After photo-excitation, SF generates the quintet state ^{5}(TT) of the two triplet pairs followed by singlet-quintet mixings. J denotes the exchange coupling.

Nagashima, H., Kawaoka, S., Matsui, Y., Tachikawa, T., Ikeda, H., & Kobori, Y. (2018). Time-Resolved EPR Study on Singlet-Fission Induced Quintet Generation and Subsequent Triplet Dissociation in TIPS-Phenyl-Tetracene

Aggregates. *Journal of Photopolymer Science and Technology*, *31*(2), 163-167.

Several reviews of SF;

Smith, M. B., & Michl, J. (2013). Recent advances in singlet fission. *Annual review of physical chemistry*, *64*, 361-386.

Smith, M. B., & Michl, J. (2010). Singlet fission. *Chemical reviews*, *110*(11), 6891-6936.

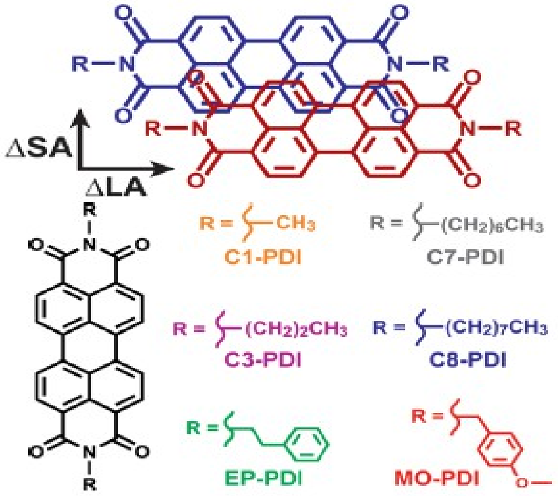
Since these two reviews, numerous SF publications and patents have appeared.

As I understand SF, it can be visualized with various versions of the Yablonski diagrams. They show a So exiton promoted to S1 which if SF would work, should be 2x the energy of the resulting triplets. If a duplicate molecule is orientated appropriately next to the S1 molecule, T1 triplets can by intersystem transfer appear on both molecules. Said triplets can generate exitons, thus one photon of the right energy can generate two triplet exitons of lower energy. This lower energy can be in the visible. Thus if you had a SF layer above a OPV, it could shower the OPV with additional exitons resulting in breaking through the Shockley−Quiesser 33% PCE limit. This then could result in PCE's higher than now possible. In fact this is what is being proposed for even silicone PV's.

Futscher, M. H., Rao, A., & Ehrler, B. (2018). The Potential of Singlet Fission Photon Multipliers as an Alternative to Silicon-Based Tandem Solar Cells. *ACS energy letters*, *3*(10), 2587-2592.

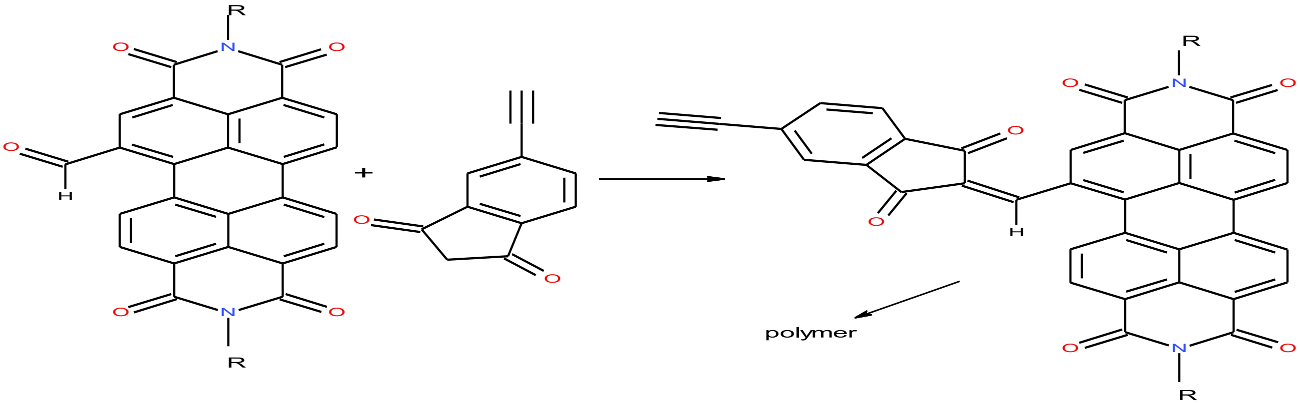
As an Organic/Polymer synthesis chemist, I really like SF because it requires organic chemistry and can be applied to all PV's. OPV's on the other hand are making progress but are far behind the inorganic PV's but have the potential advantage of cost and printable thin films. However, with SF it is possible for OPV's to break through the PCE of 14% now to possibly 20% or more. Possibly solving the need for cheap power with little or no pollution.

Of all the SF compounds now known, one type based on PDI and related structures seems tailor made for SF/OPV applications.



Le, A. K., Bender, J. A., Arias, D. H., Cotton, D. E., Johnson, J. C., & Roberts, S. T. (2018). Singlet Fission Involves an Interplay between Energetic Driving Force and Electronic Coupling in Perylenediimide Films. *Journal of the American Chemical Society*, *140*(2), 814-826.

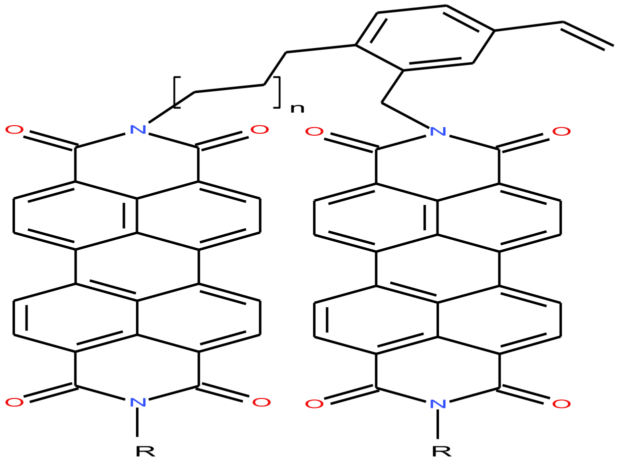
This rather detailed and informative reference, illustrates how the R group of the amide plays a critical roll in the orientation of crystalline films of the PDI compounds. Ones that extend the LA spacing and not the SA spacing result in much higher SF. My proposal is to link these PDI's to a polymer backbone with the correct orientation and spacing.



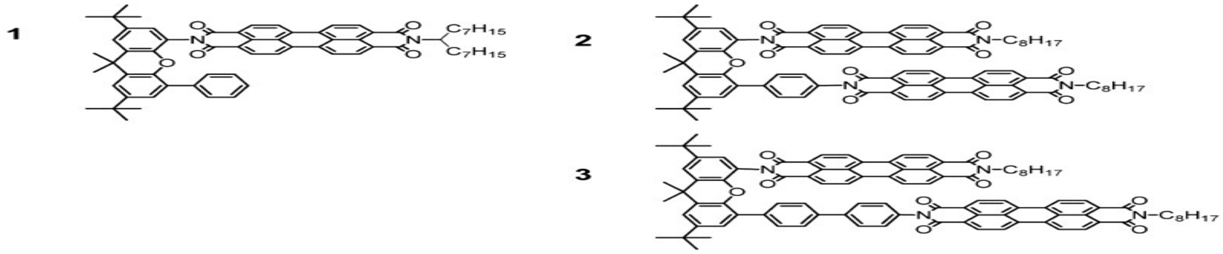
Scheme 5: Example of PDI attached to unsaturated backbone. I don't think this is a good idea because there is no guarantee that two PDI's would by chance be next to each other and in the correct orientation for SF.

Margulies, E. A., Logsdon, J. L., Miller, C. E., Ma, L., Simonoff, E., Young, R. M., ... & Wasielewski, M. R. (2016). Direct observation of a charge-transfer state preceding high-yield singlet fission in terrylenediimide thin films. *Journal of the American Chemical Society*, *139*(2), 663-671.

Examples of other PDI type structures are as follows:

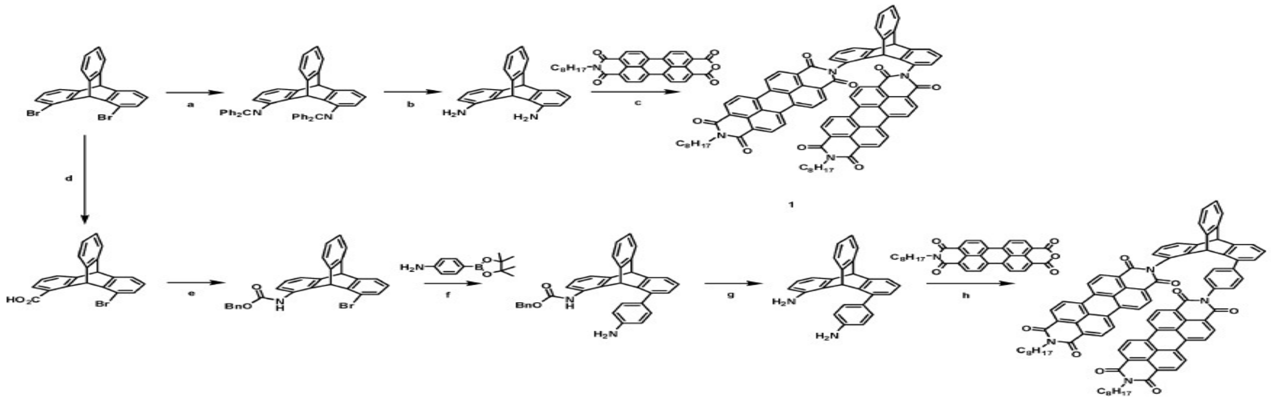


Scheme 6: This structure illustrates a monomer that has the slip stack orientation and can be polymerized. Alkyl chains are shown connecting to the vinyl substituted aromatic but other linker types such as aromatics are not excluded. This idea was derived from several references, for example:

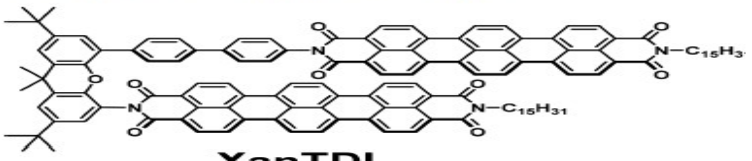


igure 1. Structures of molecules used in this study.

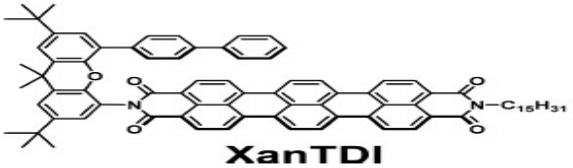
Lefler, K. M., Brown, K. E., Salamant, W. A., Dyar, S. M., Knowles, K. E., & Wasielewski, M. R. (2013). Triplet state formation in photoexcited slip-stacked perylene-3, 4: 9, 10-bis (dicarboximide) dimers on a xanthene scaffold. *The Journal of Physical Chemistry A*, *117*(40), 10333-10345.



Margulies, E. A., Shoer, L. E., Eaton, S. W., & Wasielewski, M. R. (2014). Excimer formation in cofacial and slip-stacked perylene-3, 4: 9, 10-bis (dicarboximide) dimers on a redox-inactive triptycene scaffold. *Physical Chemistry Chemical Physics*, *16*(43), 23735-23742.



XanTDI$_2$



XanTDI

Mandal, A., Chen, M., Foszcz, E., Schultz, J. D., Kearns, N. M., Young, R. M., ... & Wasielewski, M. R. (2018). Two-Dimensional Electronic Spectroscopy Reveals Excitation Energy-Dependent State Mixing during Singlet Fission in a Terrylenediimide Dimer. *Journal of the American Chemical Society*.

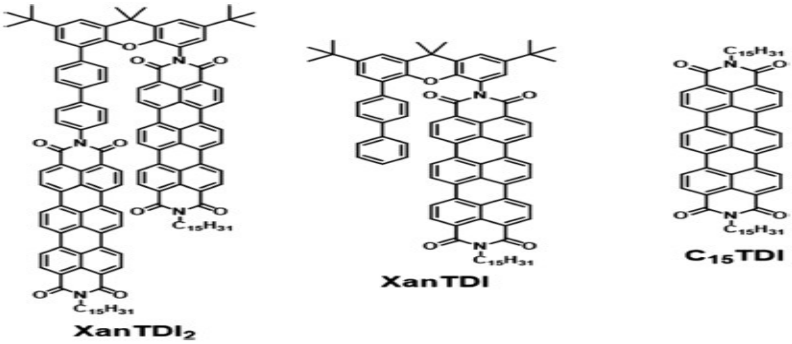
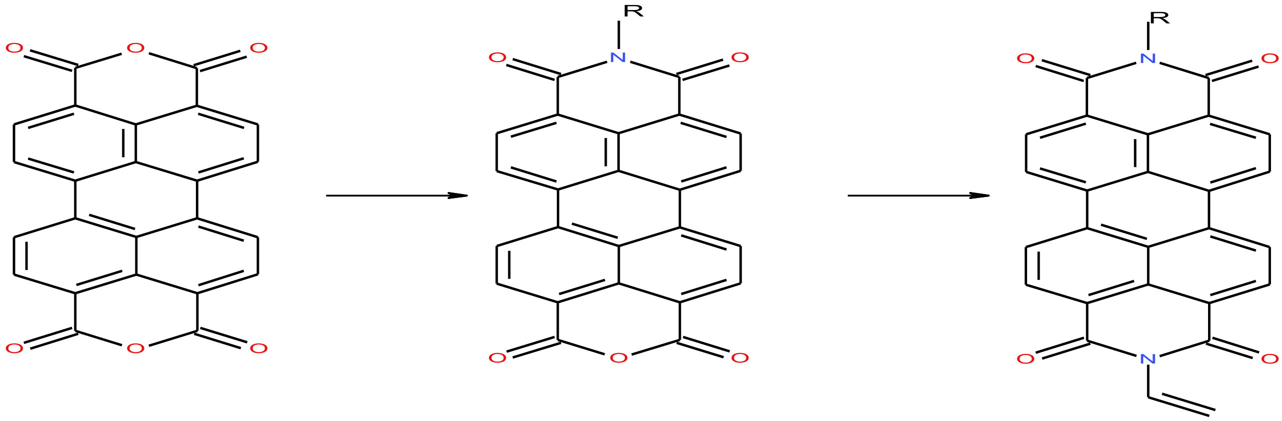


Figure 1. Chemical structures of the xanthene TDI dimer (**XanTDI$_2$**), xanthene TDI monomer (**XanTDI**), and C_{15} TDI monomer (**C_{15}TDI**).

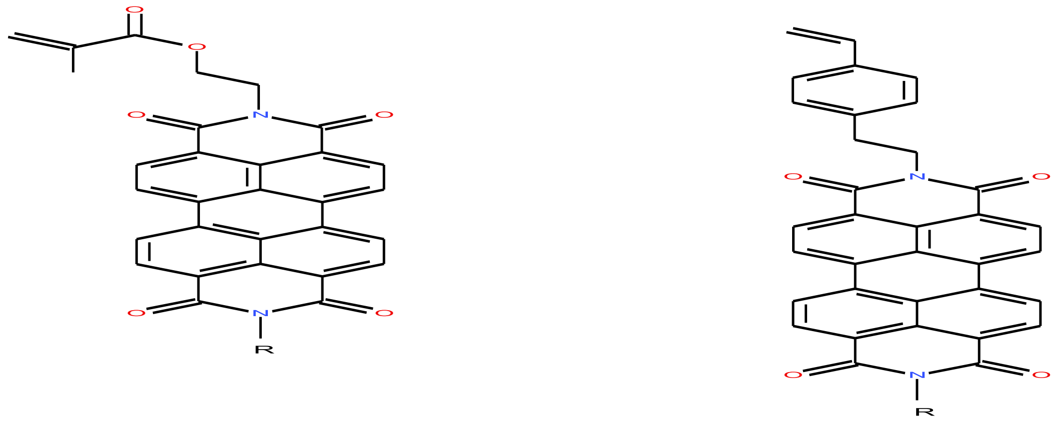
Eaton, S. W., Shoer, L. E., Karlen, S. D., Dyar, S. M., Margulies, E. A., Veldkamp, B. S., ... & Wasielewski, M. R. (2013). Singlet exciton fission in polycrystalline thin films of a slip-stacked perylenediimide. *Journal of the American Chemical Society*, *135*(39), 14701-14712.

Prof. Wasielewski has an interesting video on U-Tube concerning slip-stacked PDI's. https://www.youtube.com/watch?v=mamPzjhEkvY&t=2018s

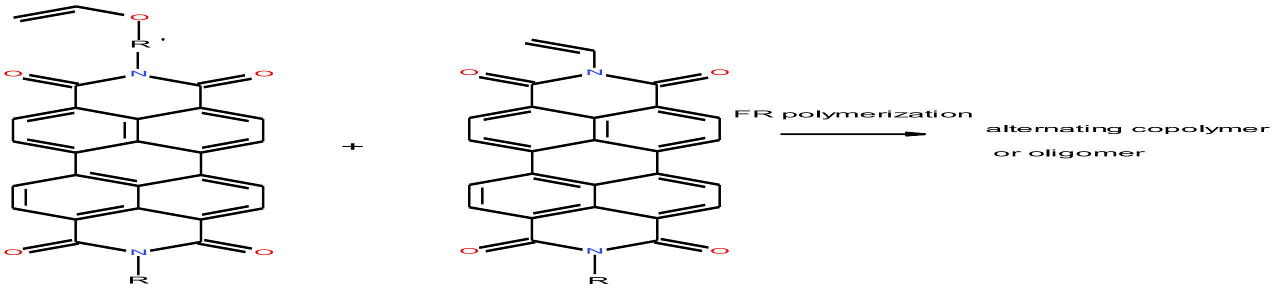


Scheme 7: N-vinylimides are polymerizable monomers. The R groups can be varied to result in slip-stacked packing in the polymeric film. Copolymers with different R groups could afford such a slip-stacked films.

Other monomers are conceivable;



Scheme 8: Other monomers.



Scheme 9: Vinyl ethers will form alternating polymers with vinyl imides in analogy with

maleic anhydride as in the Gantrez copolymers(Ashland). Such alternating copolymers would, have syndiotactic structures? Obviously isotactic polymers would be desired. Finally, polymeric SF candidates would be more mixable with polymeric donors.

In conclusion, this is a very complicated field. My problem is that in the literature, SF of rylenes depends on the slip-stacked **crystalline** structure of the SF layer. A polymeric version my not form this structure but would probably be amorphous. I could not find a reference to a polymeric version of SF PDI's types? If this idea would work then thin films would be easily coated on substrates with out the need for such crystals.

Thank you for reading this proposal!
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