

[2,2]Paracyclophane and Singlet Fission

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Singlet Fission research is currently very active because it is believed to be a method to overcome the Shockley–Queisser 33% PCE limit, bring it up to 44%. This would give OPV's a big boost. SF requires organic/polymer chemistry, while the other solar cell technologies besides OPV are silicone or lead based. SF can also apparently work to improve both silicone and lead photovoltaics. SF therefore appeals to Organic/Polymer chemists like me.

A current problem is the relatively few high performance SF compound examples. It is suggested that if more SF candidates can be made available, faster progress could be made in fundamental understanding resulting in higher OPV PCE's.

I believe that I have a good basic understanding of SF. However, I have done my best to present ideas that as an Organic/Polymer chemist seem to correlate with my understanding. I have also presented wherever I could documentation. Please look at my previous proposal “**Indane-1,3-dione Based Vinyl and Alkyne and Singlet-Fission based Polymers**” which is available on my web page.

Before going any further let me suggest several recent review articles that detail what SF is all about.

Japahuge, A., & Zeng, T. (2018). Theoretical studies of singlet fission: searching for materials and exploring mechanisms. *ChemPlusChem*, 83(4), 146-182.

“While the alleged reason for studying singlet fission in nearly every paper published recently has been to increase the efficiency of solar energy conversion, achieving this in practice has remained challenging and elusive. The demonstration of quantum efficiency in singlet fission solar cells above 100% in narrow wavelength windows has been an exciting step, and efforts are underway to use singlet fission chromophores to sensitize conventional solar cells. However, the power conversion efficiencies of all solar cells incorporating singlet fission reported to date have been far below those of conventional single junction solar cells. Among the many challenges in implementing singlet fission for solar energy conversion is the limited choice of molecules exhibiting high singlet fission yields, the limited approaches for the efficient harvesting of resulting triplets or triplet pairs, the lack of

understanding or control of how charge separation or triplet energy transfer occurs across material interfaces, and the mismatch in the long-term stability of singlet fission molecules”

above from:

Miyata, K., Conrad-Burton, F. S., Geyer, F. L., & Zhu, X. Y. (2019). Triplet Pair States in Singlet Fission. *Chemical reviews*.

Casanova, D. (2018). Theoretical modeling of singlet fission. *Chemical reviews*, 118(15), 7164-7207.

Gish, M. K., Pace, N. A., Rumbles, G., & Johnson, J. C. (2019). Emerging Design Principles for Enhanced Solar Energy Utilization with Singlet Fission. *The Journal of Physical Chemistry C*.

In my previous proposal, I reviewed the very interesting papers from Prof. Wasielewski group where PDI compounds through synthesis are ideally orientated in a slip-stacked crystal configuration to maximize SF:

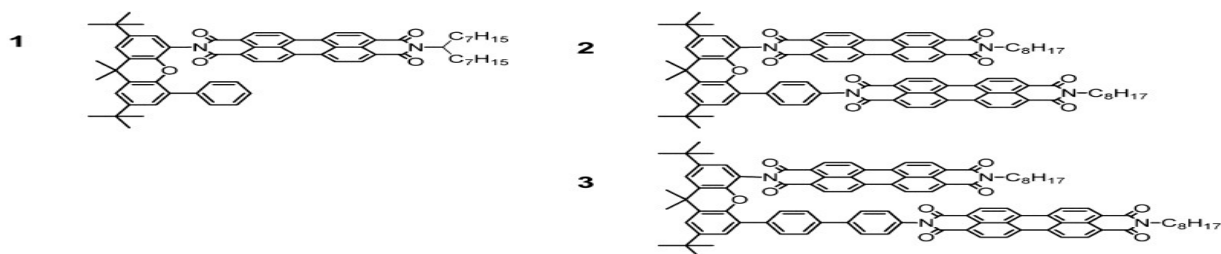
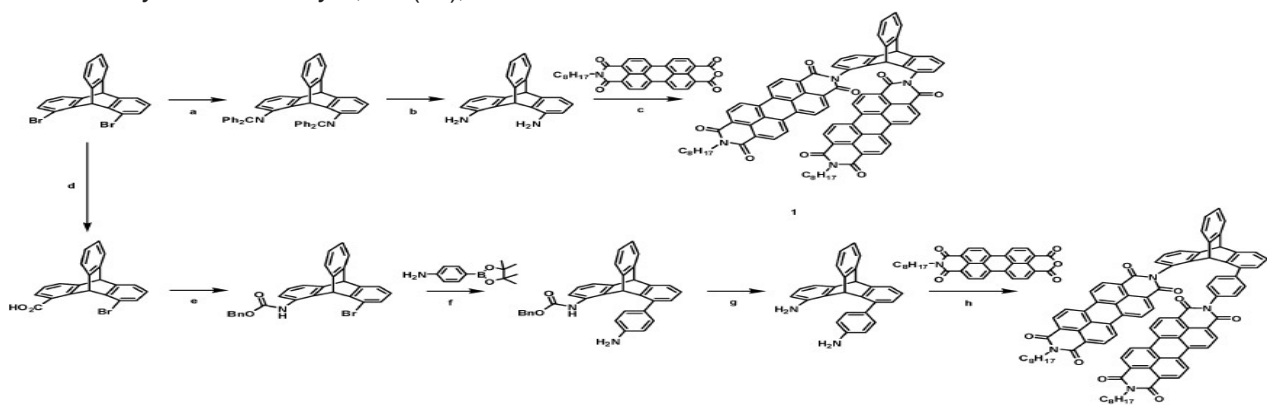
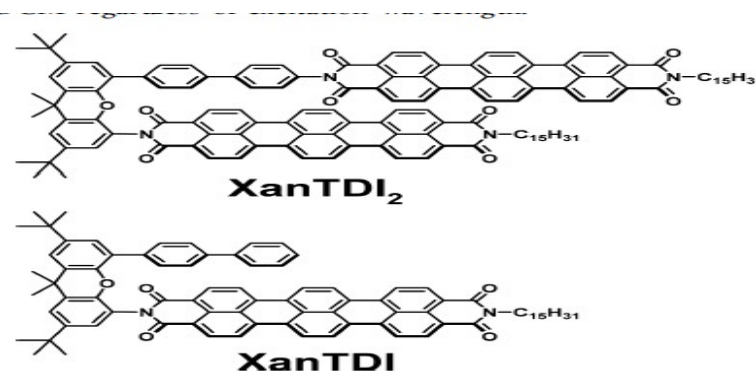


Figure 1. Structures of molecules used in this study.

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.



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*.

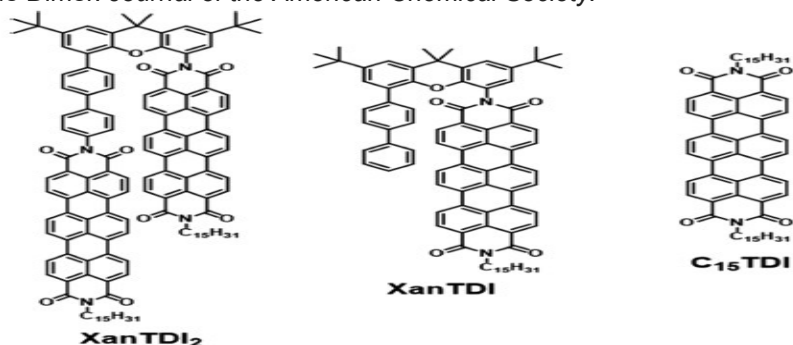


Figure 1. Chemical structures of the xanthene TDI dimer (XanTDI₂), xanthene TDI monomer (XanTDI), and C₁₅ TDI monomer (C₁₅TDI).

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>

Notice that the above examples are all homoconjugated(see explanation further on).

In the above, they show the PDI examples, arranged in non-ideal to ideal slip-stacked positions in subsequent crystal lattices which results in much better SF. PDI or rylenes in general are favorable SF candidates because unlike the large aromatic types, they are oxidatively stable, easy to synthesize and inexpensive.

For more slip-stack orientation information:

Hestand, N. J., & Spano, F. C. (2018). Expanded theory of h-and j-molecular aggregates: The effects of vibronic coupling and intermolecular charge transfer. *Chemical reviews*, 118(15), 7069-7163.

PDI's arranged in their crystalline lattices in slip-stack orientation even though they are not in direct conjugation are very active SF moieties. Two triplets can appear one on each associated PDI from the reaction of one high energy photon with only one of the

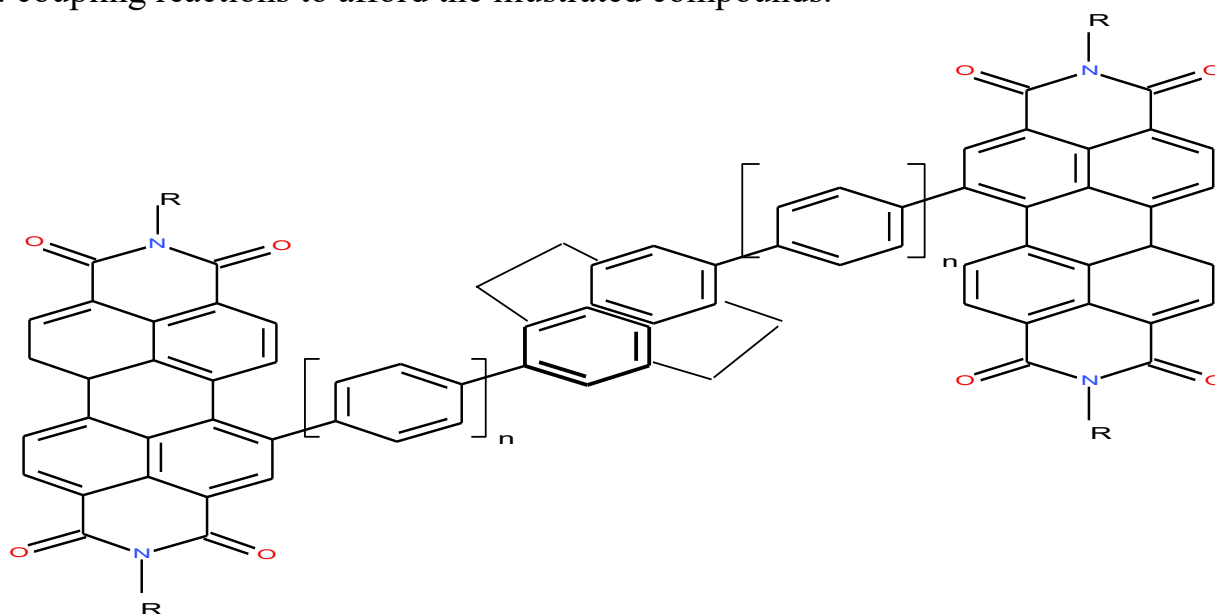
associated PDI's. This photon should have at least 2X the energy of each resulting triplet. Said triplets can then generate excitons that BHJ OPV can separate into electrons and holes.

Therefore, high energy photons instead of being dissipated as heat can add to the PCE.

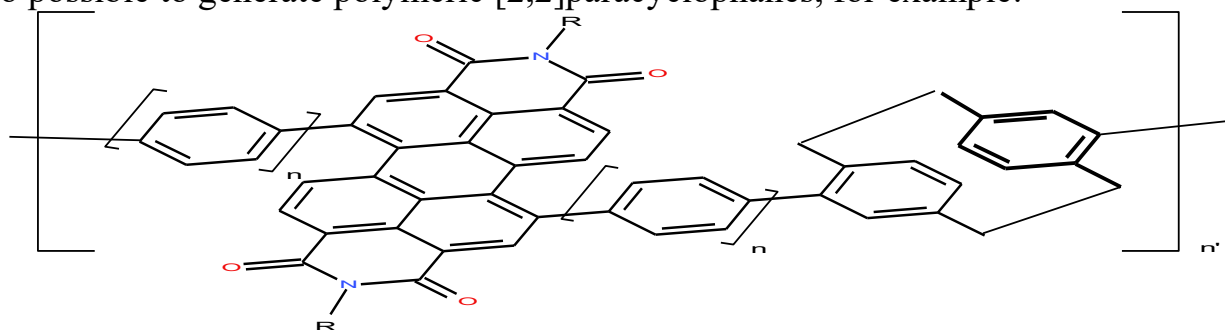
My idea is to employ [2,2]paracyclophanes in SF motifs.

Proposals:

The following schemes illustrates [2,2]paracyclophanes that can be synthesized by coupling readily available Br [2,2]paracyclophanes derivatives with Stille or Suzuki or etc. coupling reactions to afford the illustrated compounds.

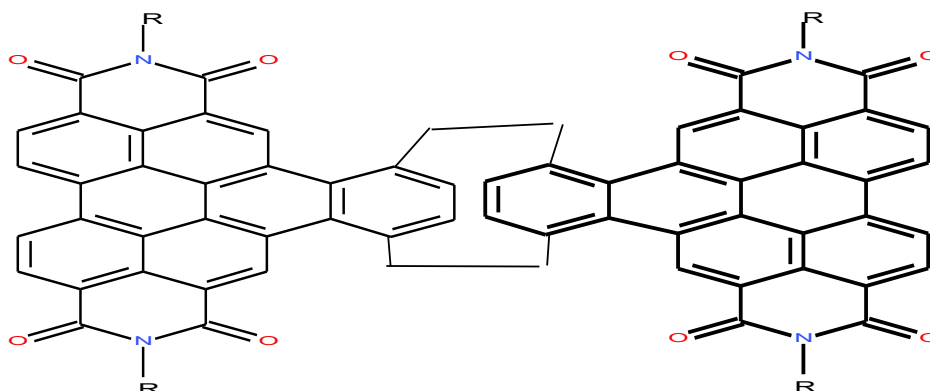


Scheme 1: This shows a compound that can have duplicate or different side chains with different n's or the benzene coupling moieties can be replaced with other unsaturated R groups or one or both PDI's can be connected directly to the [2,2]paracyclophane. The [2,2]paracyclophane isolates each associated PDI but provides “homoconjugation”. It is also possible to generate polymeric [2,2]paracyclophanes, for example:



Scheme 2: Polymeric version prepared by one or another of the well known coupling reactions. These PDI's can be considered to be “homoconjugated” as the reference below

suggests.



Scheme 3: [2,2]paracyclophane PDI. In these cases (Schemes 1-3) the two PDI's are not directly conjugated but could be considered homoconjugated.

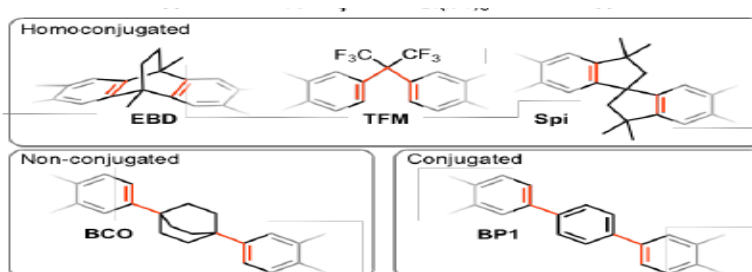
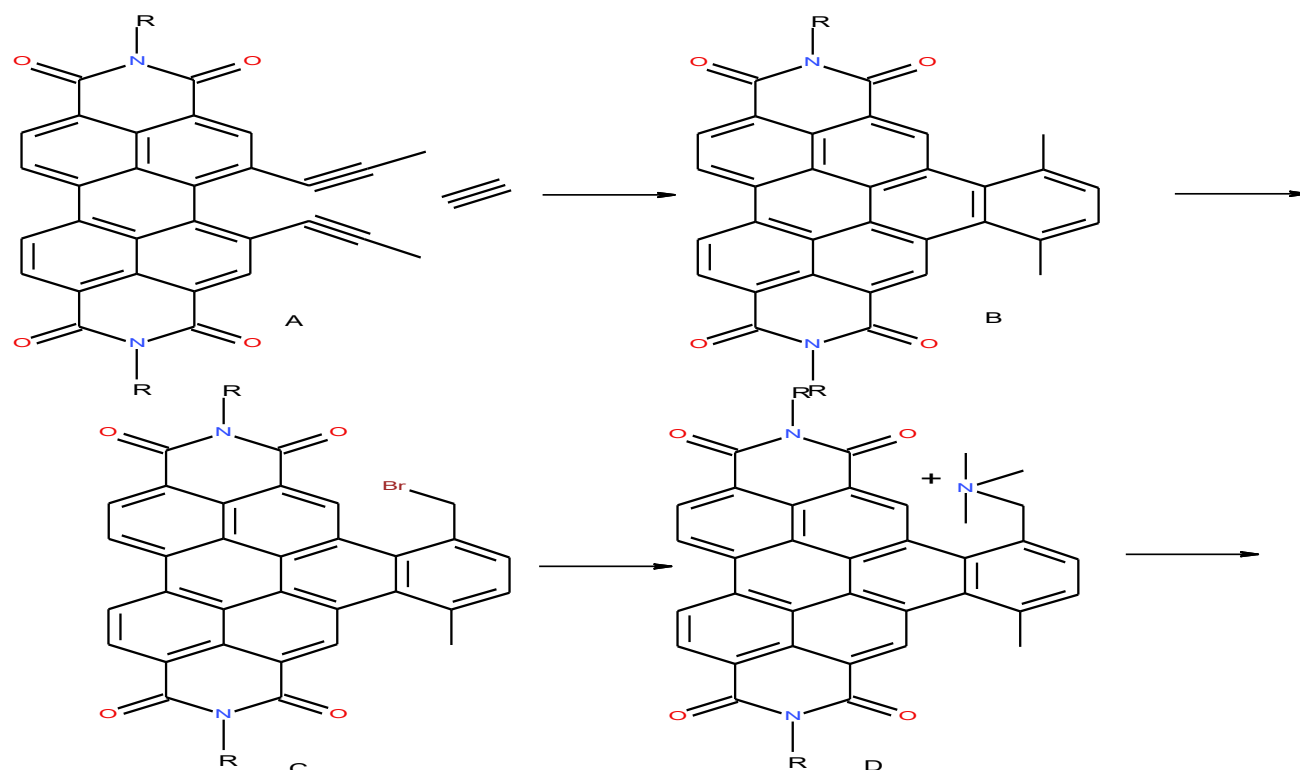


Figure 1. The pentacene-bridge-pentacene model showing the comparison between different bridging units. In the bottom representations, the pentacenes are omitted to highlight the nature of the bridging units.

Conclusions: Through the evaluation of a family of materials, we have found that the conjugation motif of the interpentacene bridge is instrumental in mediating singlet fission in pentacene dimers. The concept of intrachromophore coupling interactions in π -bridge- π molecules was tested using homoconjugated and non-conjugated bridging moieties. In these systems, homoconjugated bridges can yield singlet fission rates that are faster than a conjugated bridge, while maintaining slower triplet pair recombination. We also found that SF can occur in the case of a non-conjugated bridge, although the process is much slower than SF in a similar sized conjugated bridge. We further characterized the formation of triplet pairs through singlet fission using ESR measurements. This study demonstrates the importance of the bridge design in such compounds and emphasizes that bridge effects must play a key role in understanding SF and triplet pair recombination.

Kumarasamy, E., Sanders, S. N., Tayebjee, M. J., Asadpoordarvish, A., Hele, T. J., Fuemmeler, E. G., ... & Dean, J. C. (2017). Tuning singlet fission in π -bridge- π chromophores. *Journal of the American Chemical Society*, 139(36), 12488-12494.



Scheme 4: Conceivable synthesis of scheme 3. Compound A is the Sonogashira Coupling of the dibromo bay PDI derivative. I didn't indicate the transmetal catalyst needed for the 2+2+2 aromatic synthesis and I show the acetylene in its simplest form. Hoffman(Winberg) elimination of D generates the intermediate that dimerizes to the [2,2]paracyclophane. This chemistry has been well documented in numerous patents and articles.

Chow, H. F., Low, K. H., & Wong, K. Y. (2005). An improved method for the regiospecific synthesis of polysubstituted [2,2] paracyclophanes. *Synlett*, 2005(14), 2130-2134.

Hartner, H. (1985). *U.S. Patent No. 4,532,369*. Washington, DC: U.S. Patent and Trademark Office.

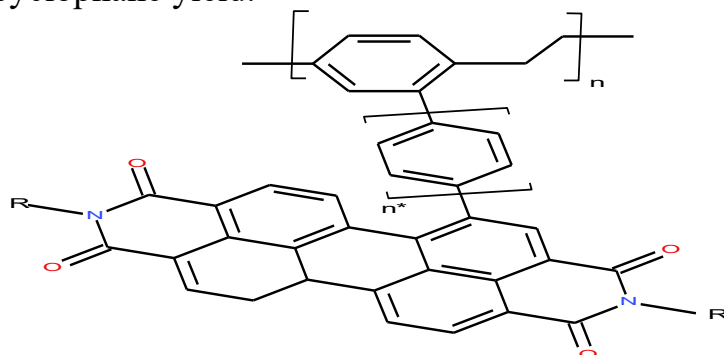
Otsubo, T., Mizogami, S., Otsubo, I., Tozuka, Z., Sakagami, A., Sakata, Y., & Misumi, S. (1973). Layered compounds. XV. synthesis and properties of multilayered cyclophanes. *Bulletin of the Chemical Society of Japan*, 46(11), 3519-3530.

In the Hofmann elimination, a quaternary ammonium group is the leaving group but because it is ionic there might be a problem with solubility with PDI's especially in polar solvents; therefore, further on in these proposals I will discuss other alternative leaving groups.

Also the yields of [2,2]paracyclophanes by the Winberg method are usually modest at best, but efficient SF of said compounds would encourage the search for improvements.

Polymer instead of [2,2]paracyclophane

One might suggest a Gilch reaction where the polymer is obtained directly as the desired product. The [2,2]paracyclophane synthesis tries to avoid polymers by employing antioxidants because the polymerization is by a free radical mechanism. The patent literature illustrates how to minimize polymerization and maximize [2,2]paracyclophane yield.

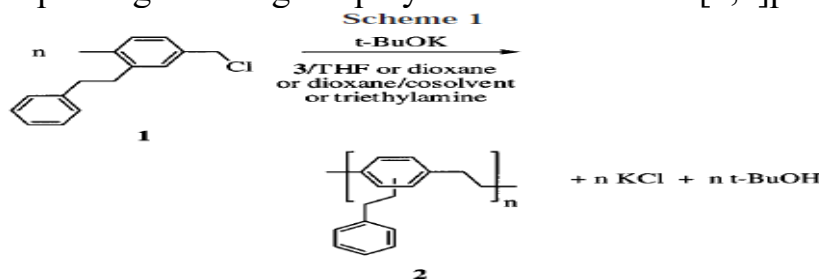


Scheme 5: Why fight the formation of polymers? They appear to be favored and are suppressed with free radical traps like phenothiazine in order to obtain modest yields of the [2,2]paracyclophanes.

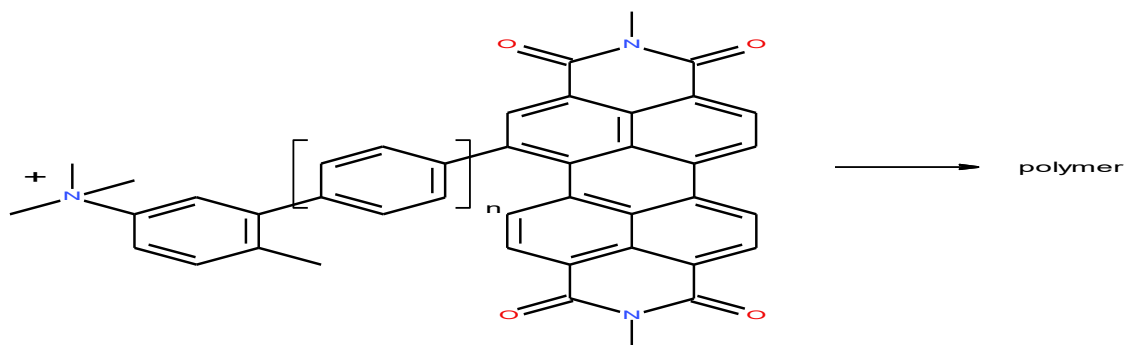
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Citations

Here is an example of generating the polymer instead of the [2,2]paracyclophane.



Brink-Spalink, F., & Greiner, A. (2002). Efficient Control on Molecular Weight in the Synthesis of Poly (p-xylylene) s via Gilch Polymerization. *Macromolecules*, 35(9), 3315-3317.



Scheme 6: My idea for a typical monomer. Obviously other examples that includes rylenes in a Hofmann elimination context should also be considered. Note that a chloride

could replace the quat in the Gilch method.

The quat necessary for the Hofmann elimination is probably unsuitable for this polymerization because of the probable poor solubility of the monomer in aqueous or highly polar solutions. A better idea would be to replace the quat with a polar nonionic leaving group that would result in organic solvent solubility.

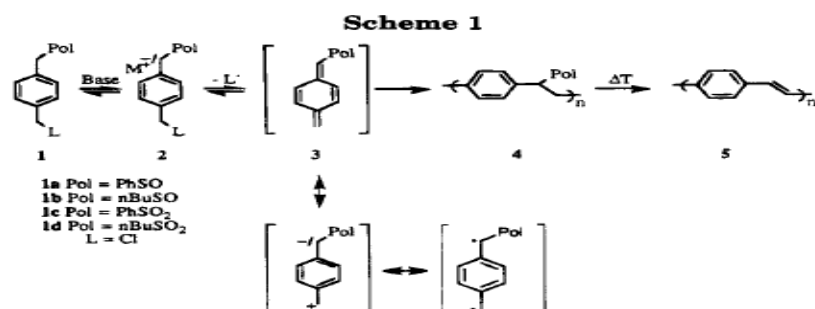


Table 1. Molecular Weight Values^a for the Polymerization of Monomers with Different Polarizers in NMP

polarizer	$M_p (\times 10^5)^b$	$M_n (\times 10^5)$	$M_w (\times 10^5)$	yield ^c (%)
PhSO	0.5	0.24	0.64	47
nBuSO	3.0	0.69	3.0	37
PhSO ₂	5.0	2.40	4.30	71
nBuSO ₂	2.0	0.91	4.20	46
nBuSO ₂ ^d	21.5	4.84	29.30	53

^a Molecular weight values were measured with GPC in NMP against polystyrene standards. ^b M_p = molecular weight at peak maximum. ^c Yield of the high molecular weight fraction. ^d DMF was used as solvent instead of NMP.

Louwet, F., Vanderzande, D., Gelan, J., & Mullens, J. (1995). A new synthetic route to a soluble high molecular weight precursor for poly (p-phenylenevinylene) derivatives. *Macromolecules*, 28(4), 1330-1331.

Unlike this reference, the xylene would be monosubstituted with a neutral electron withdrawing polar group. Elimination can then be conducted with a powerful base like sodium hydride in a suitable solvent. I refer the reader to the extensive Poly-(p-phenylenevinylene)(PPV) literature that makes use of difunctional derivatives of para-xylenes for more information. I would employ the PPV difunctional xylenes derivative types as mono substituted xylenes resulting in saturated polymeric ethane linkages rather than ethylenes as in the PPV's.

Müllen, K., Reynolds, J. R., & Masuda, T. (Eds.). (2013). *Conjugated polymers: a practical guide to synthesis*. Royal Society of Chemistry.

Leclerc, M., & Morin, J. F. (Eds.). (2010). *Design and synthesis of conjugated polymers*. John Wiley & Sons.

Although there are many routes to Poly-(p-phenylenevinylene)(PPV)'s, I believe that conjugating these PDI (or rylene)s like PPV would not facilitate SF but having them separated by ethane units would be very beneficial.

Thank you for reading these proposals!

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