

## New Polymeric Organic Solar Cells

By: Robert B. Login rloginconsulting

So far this year I've tried to look at over 600 2018 references to OPV's and especially NFA(non-fullerene acceptors) of various compositions.

### **Molecular optimization enables over 13% efficiency in organic solar cells**

[W Zhao, S Li, H Yao, S Zhang, Y Zhang...- Journal of the..., 2017 - ACS Publications](#)

A new polymer donor (PBDB-T-SF) and a new small molecule acceptor (IT-4F) for fullerene-free organic solar cells (OSCs) were designed and synthesized. The influences of fluorination on the absorption spectra, molecular energy levels, and charge mobilities of the...

[Cited by 840](#)(over 600 in 2018).

I want to give the reader an idea of OPV technology. I am not claiming I know the in depth physics of these donor polymer/A-D-A NFA's but this is what I understand. There are three factors that determine the PCE(efficiency), the Voc(open circuit voltage), the Jsc(short circuit current) and the FF(fill factor). The first two are associated with the Homo and Lumo energy levels of the donor polymer and the NFA such that to get the highest PCE requires that the absorption, in the whole or most of sunlight's spectrum, is productively captured. This is best when the NFA has a narrow band gap and the electron and hole conductivity is matched between the donor polymer and the NFA. The Voc is related to the energy gap between the donor and acceptor LUMOs, with the acceptor more negative than the donor. This driving force difference between the energy levels is subtracted from the possible max Voc. The Voc also depends on the fill factor, the depth of the curve of voltage vs current, which is highly influenced by the morphology of the resulting BHJ phase separation and the distance the electrons and holes have to hop to be effective. The more face on crystalline the NFA, the higher the ff and the Voc. So if the donor polymer phase BHJ is close enough to the NFA crystalline regions the easier the conversion of the resulting excitons to form electrons that can be captured by the NFA which then can deliver them to the cathode. Holes are retained by the donor polymer and are delivered to the anode to complete the circuit. Excitons can dissociate also in the acceptor because photons can interact directly with the acceptor. The acceptor then can move holes to the donor and the electrons to the cathode. These excitons and subsequent holes and electrons can recombine or they can be trapped by imperfections or by the distance to the appropriate phase. Even with this complicated situation, PCE's of 14% have been achieved.

By the number of current references, it is obvious that there's a lot that is still unknown.

### **Three Components**

Currently there is interest in combining multiple components in said OSC's. Especially interesting is employing one donor polymer with two NFA's. The reasoning is that more

of the sun's spectrum can be captured and the two NFA's can both form xtal regions to improve  $J_{sc}$  and  $J_{ff}$ . With this approach, high PCE's have been achieved.

**Table 1.** Recent progress in ternary nonfullerene PSCs.

Ternary system	Binary blend [D:A]	PCE [%]	The third component	PCE [%]	Reference
D1:A1:A2	PTB7-Th:ITIC-Th	8.25	FT-2PDI	8.87	[17]
	PTB7-Th:ITIC-Th	8.10	FBR-CN	9.82	[18]
	PTB7-Th:IDT-2BR	8.5	PDI-2DTT	10.1	[19]
	PDBT-T1:SdiPBI-Se	8.15	ITIC-Th	10.27	[20]
	PBDB-T:ITIC-Th	9.75	TPE-4PDI	10.82	[17]
	PCE10:IDTBR	–	IDFBR	11.0	[21]
	PSTZ:ITIC	8.06	IDIC	11.1	[22]
D1:D2:A	J52:IT-M	9.4	IEICO	11.1	[23]
	PSEHTT:DBFI-EDOT	8.1	PBDTT-FTTE	8.52	[24]
	PTB7-Th:PNDI-T10	7.6	PBDTTS-FTAZ	9.0	[25]
	J51:ITIC	8.89	PTB7-Th	9.70	[26]
	PBDTTT-EFT:IEICO-4F	10.0	J52	10.9	[27]
	PBDB-T:IEICO-4F	10.25	PTB7-Th	11.62	This work

Ma, X., Mi, Y., Zhang, F., An, Q., Zhang, M., Hu, Z., ... & Tang, W. (2018). Efficient Ternary Polymer Solar Cells with Two Well-Compatible Donors and One Ultra narrow Band gap Nonfullerene Acceptor. *Advanced Energy Materials*, 8(11), 1702854.

This reference shows the value of preparing OPV's with three components. Even the above 2018 paper was quickly cited by 26 references! This indicates the high level of interest in this idea.

## All Polymer OPV's

All polymeric solar cells are also of active current interest. Here morphology is the driving force as it is reasoned that polymer-polymer intimate mixing is more likely, while polymer-small molecule close mixing interactions are more problematic. All polymer OSC's have the supposed advantage that mixing of polymers can result in very close associations that upon equilibrium, forms very close separate phases making it easier for electrons and holes to hop across. This close association should produce high PCE OPV's.

McNeill, C. R., & Greenham, N. C. (2009). Conjugated-polymer blends for optoelectronics. *Advanced Materials*, 21(38-39), 3840-3850.

If this is true then in certain cases, the  $J_{ff}$  should be better and this appears to not be the current state of affairs with PDI's.

Liu, Z., Zeng, D., Gao, X., Li, P., Zhang, Q., & Peng, X. (2019). Non-fullerene polymer acceptors based on perylene diimides in all-polymer solar cells. *Solar Energy Materials and Solar Cells*, 189, 103-117.

## Single material solar cells

Currently single material solar cells are of interest. A very recent review has appeared by one of the best known workers in OSC's:

Roncali, J., & Grosu, I. (2018). The Dawn of Single Material Organic Solar Cells. *Advanced Science*, 1801026.

“In this context, the fabrication of OPV cells using only one material can present several decisive advantages. From a technical point of view, single material organic solar cells (SMOSCs) will considerably reduce the complexity and cost of cell fabrication while providing a possible definitive solution to the morphological

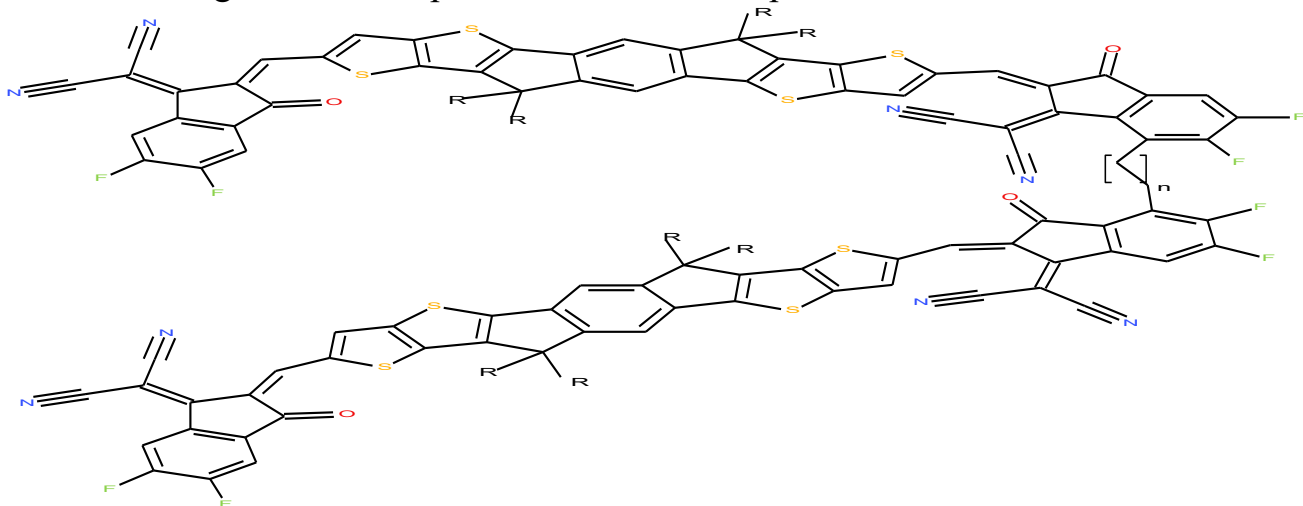
instability of multicomponent BHJs.<sup>[60]</sup> The synthesis of active materials for SMOSCs implies the association of D and A parts into molecular architectures capable to achieve the elemental processes of light absorption, exciton dissociation, and charge transport usually ensured by two different materials in BHJs. In spite of these major potential advantages, SMOSCs have, until now, attracted much less attention than BHJs. This

situation may be related to the considerable difficulty of the task and to the widespread idea that because of fast charge recombination and inefficient charge hopping and transport, SMOSCs cannot reach high PCEs.”

I will propose several ideas for such single component solar cells.

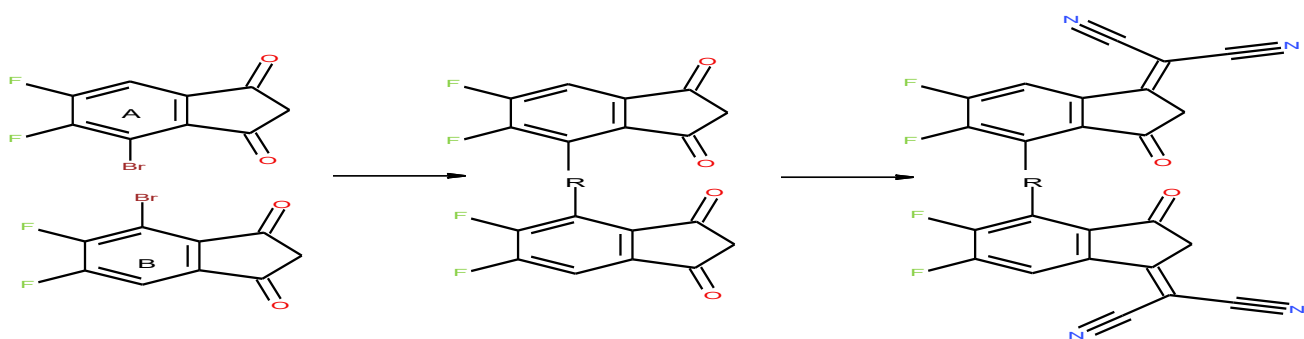
## Proposals:

What I propose is to tether or polymerize ITIC type NFAs together so that they are associated in a manner that would encourage crystallization or they can be tethered with donors resulting in SMOSCs possibilities. For example:

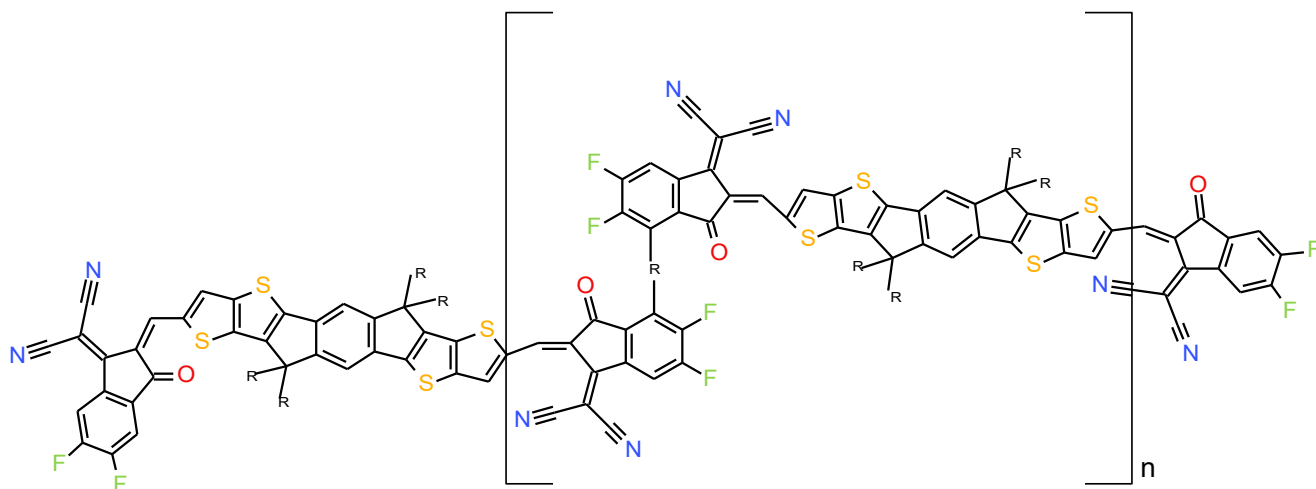


Scheme 1: This shows two identical NFA's tethered with an alkyl chain whose composition and length would determine its flexibility, when optimized it would facilitate chain to chain alignment. Note that two different NFA's can be employed to form a three component A-D-A'-D'-A'. Also A-D SMOSCs tethers are also suggested.

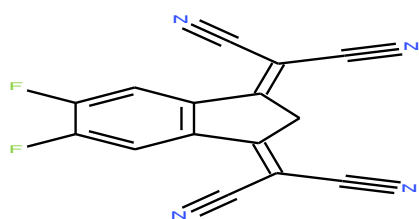
Furthermore these indanedione dimers can be used as comonomers in polymerization.



Scheme 2: The dimer can react with the usual dialdehyde donor sections of NFA's to synthesize oligomers or polymers. I think however that low MW oligomers would form crystalline regions more easily, if that's the goal. Also note that the dicyanomethylidene derivatives might have to be prepared before the dimerization to avoid placing two on the same indanedione. It should be noted that the dicyanomethylidene derivative might not be needed if the idea is to condense these dimers with both acceptors and donors in single component solar cells.



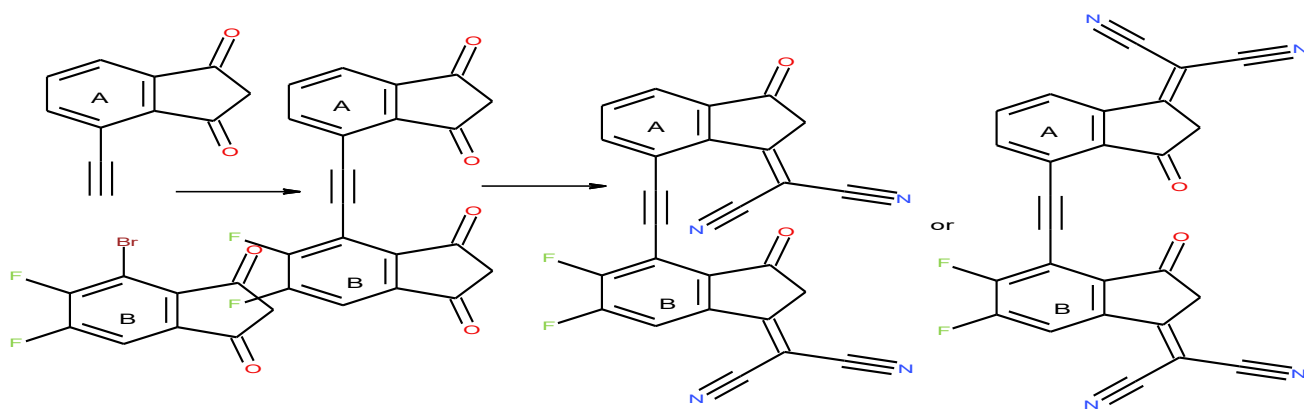
Scheme 3:  $n$  can be one or more. If one then they are tethered, more, they are oligomers or polymers. This is but one example, many more variations can be visualized.



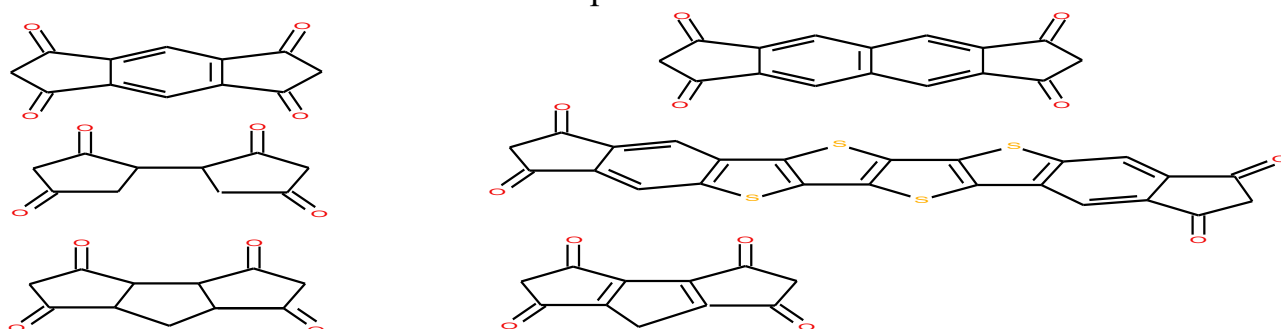
As an aside, this begs the question as to why the above bis type structure is not popular? It is known to be a very strong acceptor and it does have references.

Sun, S. S., Zhang, C., Dalton, L. R., Garner, S. M., Chen, A., & Steier, W. H. (1996). 1, 3-Bis (dicyanomethylidene) indane-based second-order NLO materials. *Chemistry of materials*, 8(11), 2539-2541.

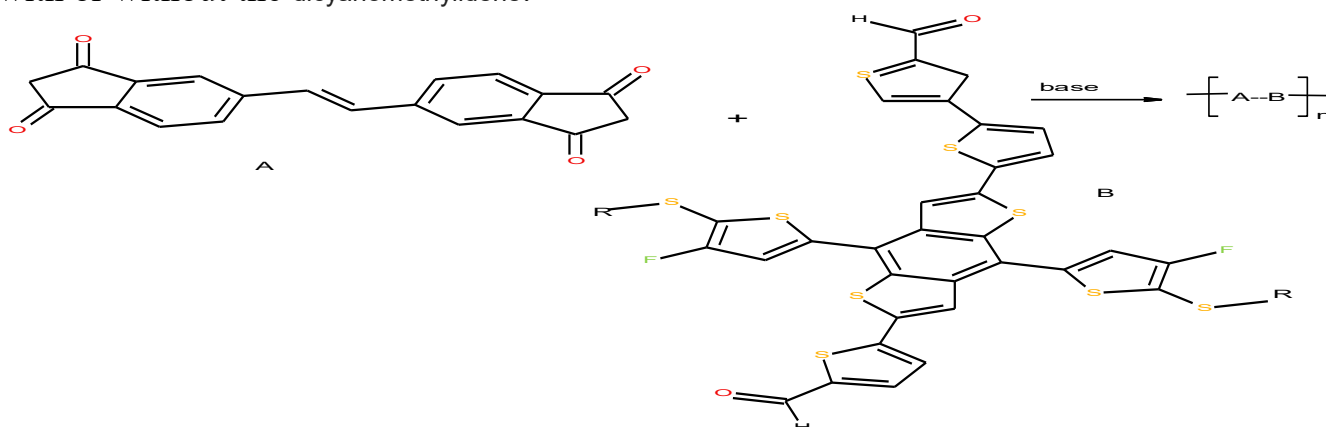
Francos, J., García-Garrido, S. E., Borge, J., Suárez, F. J., & Cadierno, V. (2016). Butadiene dyes based on 3-(dicyanomethylidene) indan-1-one and 1, 3-bis (dicyanomethylidene) indane: synthesis, characterization and solvatochromic behaviour. *Rsc Advances*, 6(9), 6858-6867.



Scheme 4: This shows that different acceptor terminals can be combined.



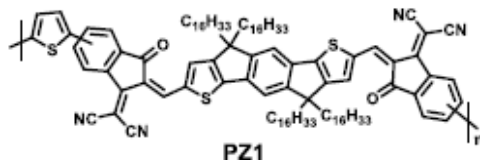
Scheme 5: Some Janus Diketone possibilities. The top two are known compounds. These ketones can condense by themselves with aldehydes by the Knoevenagel condensation; however, attaching one dicyanomethylidene to each side might be a problem because how do you prevent two on one side or does it matter? The tetraone with polythiophenes is just an example of my representation of a donor type that can be condensed with a ITIC type dialdehyde intermediate to form a A-D polymer SMOSCs with or without the dicyanomethylidene.



Scheme 6: Example of a donor polymer.

After extensive searching, I found a recent article for a related polymeric derivative like scheme 3. Although this reference was cited by 63, I only found one more reference by the same authors concerning PZ1. PZ1 is claimed to produce high PCE all polymer

OPV's.

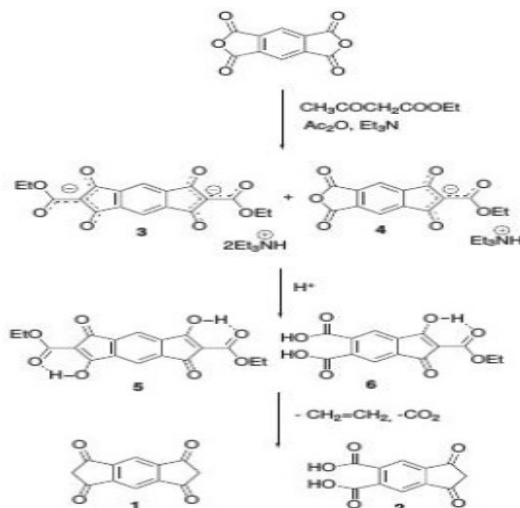


Zhang, Z. G., Yang, Y., Yao, J., Xue, L., Chen, S., Li, X., ... & Li, Y. (2017). Constructing a Strongly Absorbing Low-Bandgap Polymer Acceptor for High-Performance All-Polymer Solar Cells. *Angewandte Chemie*, 129(43), 13688-13692.

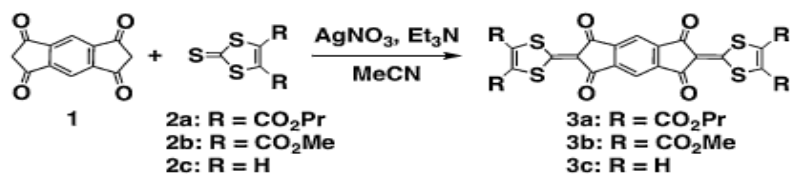
Yang, Y., Qiu, B., Chen, S., Zhou, Q., Peng, Y., Zhang, Z. G., ... & Feng, L. (2018). High-efficiency organic solar cells based on a small-molecule donor and a low-bandgap polymer acceptor with strong absorption. *Journal of Materials Chemistry A*, 6(20), 9613-9622.

### Suggested possible synthesis references:

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.

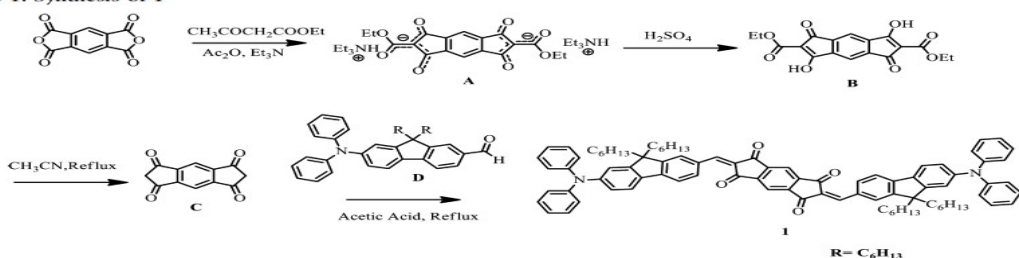


Akaike, K., Enozawa, H., Kajitani, T., Koizumi, M., Kosaka, A., Hashizume, D., ... & Fukushima, T. (2013). Tetrathiafulvalene Hybridized with Indacenetetraone as Visible-light-harvesting Electron Acceptor Applicable to Bulk-heterojunction Organic Photovoltaics. *Chemistry Letters*, 42(11), 1417-1419.

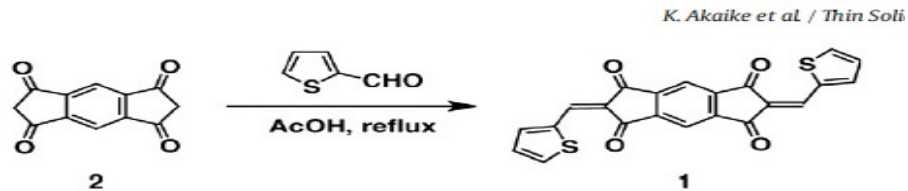


Githaiga, G. W., Woodward, A. W., Morales, A. R., Bondar, M. V., & Belfield, K. D. (2015). Photophysical and Computational Analysis of a Symmetrical Fluorene-Based Janus Dione Derivative. *The Journal of Physical Chemistry C*, 119(36), 21053-21059.

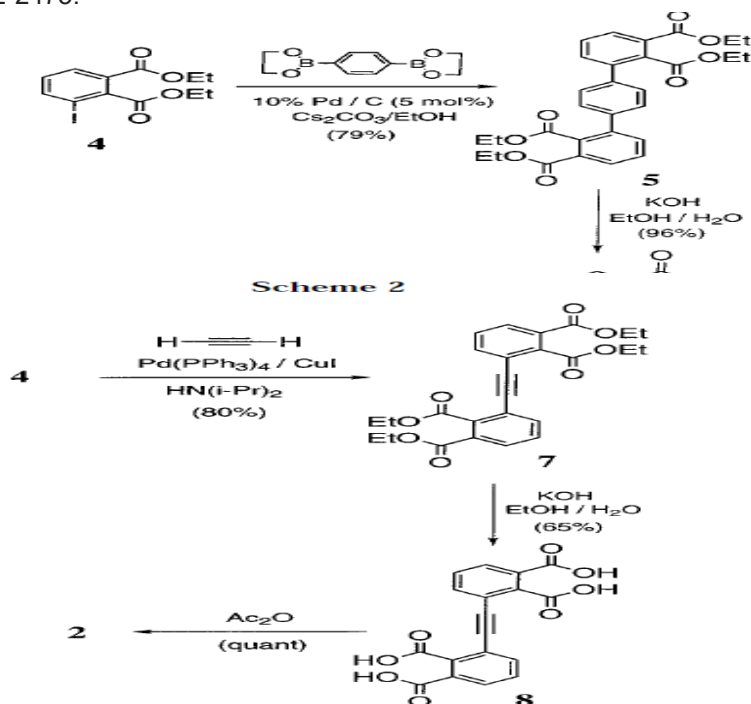
Scheme 1. Synthesis of **1**

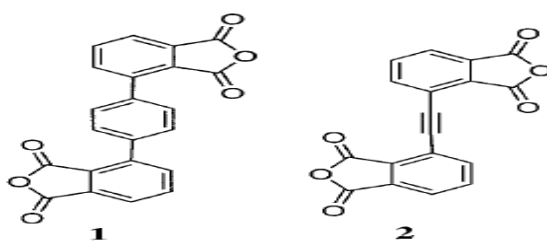


Akaike, K., Ando, S., Enozawa, H., Kosaka, A., Kajitani, T., & Fukushima, T. (2015). An electron-accepting molecular unit exhibiting an orientational preference favorable for organic photovoltaic applications. *Thin Solid Films*, 583, 34-39.



Walsh, C. J., & Mandal, B. K. (2001). A new class of aromatic dianhydrides for thermostable polyimides. *Chemistry of materials*, 13(8), 2472-2475.



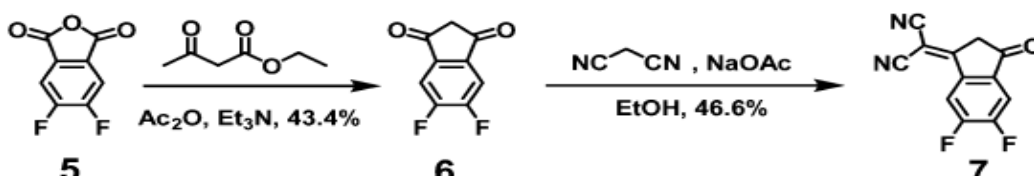


Related chemistry:



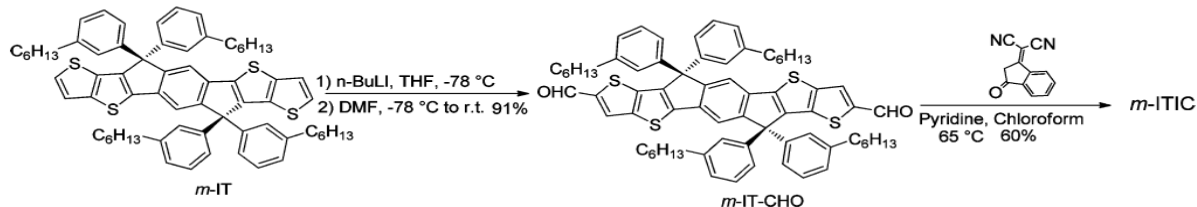
### III. TEA, $\text{Ac}_2\text{O}$ , *tert*-butyl acetoacetate;

Deng, D., Zhang, Y., Zhang, J., Wang, Z., Zhu, L., Fang, J., ... & Wei, Z. (2016). Fluorination-enabled optimal morphology leads to over 11% efficiency for inverted small-molecule organic solar cells. *Nature communications*, 7, 13740.

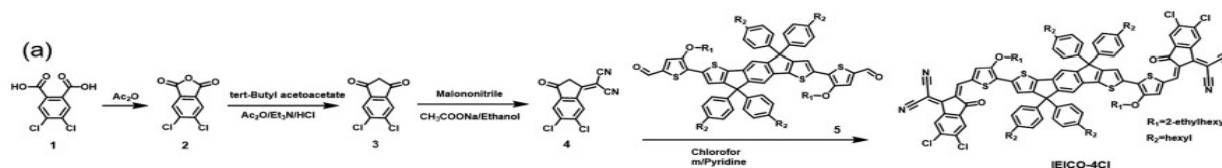


Dai, S., Zhao, F., Zhang, Q., Lau, T. K., Li, T., Liu, K., ... & Zhan, X. (2017). Fused nonacyclic electron acceptors for efficient polymer solar cells. *Journal of the American Chemical Society*, 139(3), 1336-1343.

Scheme 1. Synthetic Route of *m*-ITIC



Xue, L., Yang, Y., Xu, J., Zhang, C., Bin, H., Zhang, Z. G., ... & Yao, J. (2017). Side Chain Engineering on Medium Bandgap Copolymers to Suppress Triplet Formation for High-Efficiency Polymer Solar Cells. *Advanced Materials*, 29(40), 1703344.



Cui, Y., Yang, C., Yao, H., Zhu, J., Wang, Y., Jia, G., ... & Hou, J. (2017). Efficient Semitransparent Organic Solar Cells with Tunable Color enabled by an Ultralow-Bandgap Nonfullerene Acceptor. *Advanced Materials*, 29(43), 2017

References I could not obtain:



A general approach toward *Janus diones*: synthesis of dicyclopenta[*b,g*]naphthalene-1,3,6,8(2*H*,7*H*)-tetraone

ClaudeNiebelVladimirLokshinVladimirKhodorkovsky

<https://doi.org/10.1016/j.tetlet.2008.10.028>

## Abstract

A general approach toward *Janus diones* involving the reaction of pyromellitic or naphthalenetetracarboxylic dianhydrides with ethyl(triphenylphosphoranylidene)acetate and subsequent rearrangement of the products is described. This approach allows avoiding the formation of poorly soluble intermediates, in which purity cannot be effectively controlled. Dicyclopenta[*b,g*]naphthalene-1,3,6,8(2*H*,7*H*)-tetraone **3**, a promising precursor of molecular and polymeric advanced materials is described

2,3,6,7-Naphthalenetetracarboxylic dianhydride revisited

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## Abstract

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2,3,6,7-Naphthalenetetracarboxylic dianhydride was prepared and characterized by UV, IR, and NMR spectra. Its structure was confirmed by single crystal X-ray determination. It is a moderate strength electron acceptor, stronger than *p*-benzoquinone and weaker than pyromellitic anhydride according to quantum mechanical calculations and electrochemical measurements.

## Comparative Studies on Optical, Redox, and Photovoltaic Properties of a Series of D–A–D and Analogous D–A Chromophores

A Zitzler-Kunkel, MR Lenze, T Schnier... - *Advanced Functional...*, 2014 - Wiley Online Library

A series of new symmetrical donor-acceptor-donor (D–A–D) dyes based on *s*-indacene-1,9,5,7(2*H*,6*H*)-tetraone as an acceptor unit containing varying electron donating moieties and analogous donor-acceptor (D–A) chromophores with indane-1,3-dione as an acceptor are synthesized. By employing these two sets of dyes, the influence of a scaffold change from unsymmetric push-pull (D–A) to symmetrical (D–A–D) systems on optical, electrochemical, and photovoltaic properties are explored. Detailed comparative studies.

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## Combination of Dicyanovinylindanone (DCI)/Maleimide Acceptors

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Many of the most successful small compound acceptors are ITIC or related structures.

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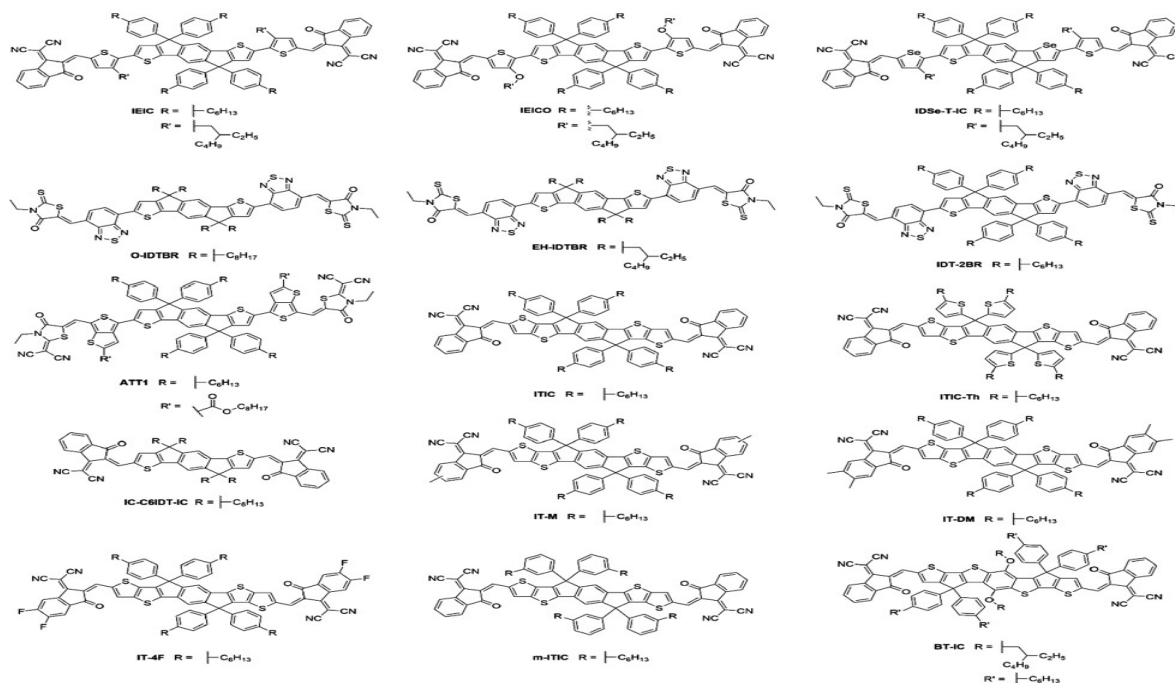
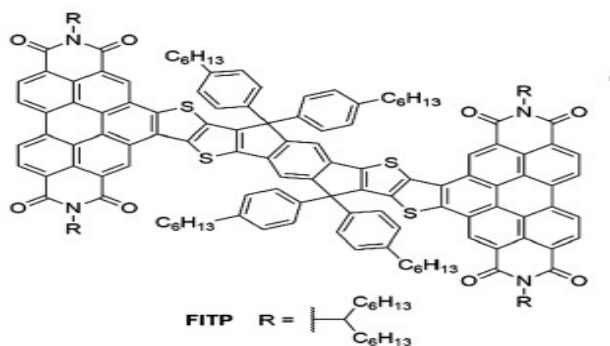


Fig. 5 IDT and IDTT based small molecule A-D-A type acceptors.

Wadsworth, A., Moser, M., Marks, A., Little, M. S., Gasparini, N., Brabec, C. J., ... & McCulloch, I. (2018). Critical review of the molecular design progress in non-fullerene electron acceptors towards commercially viable organic solar cells. *Chemical Society Reviews*.

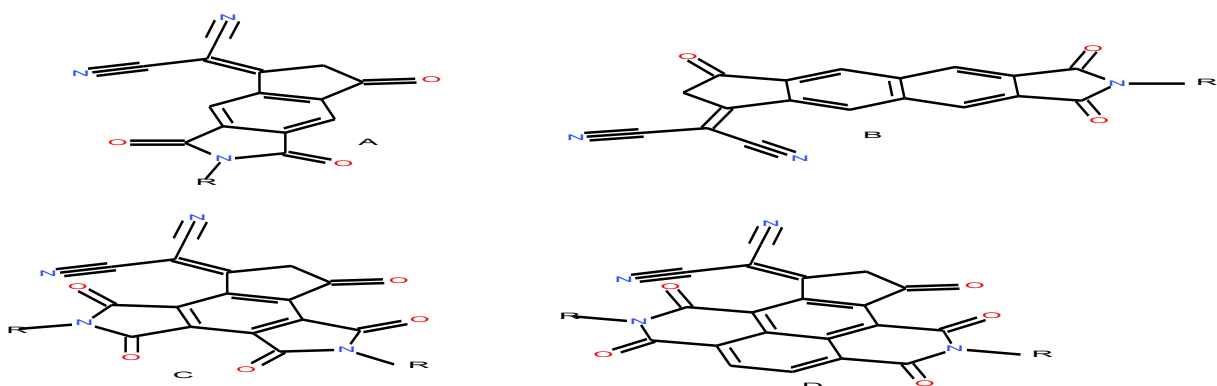
The above are indacenodithiophene and indacenodithienothiophene capped with mostly dicyanovinylindanone (DCI) groups.



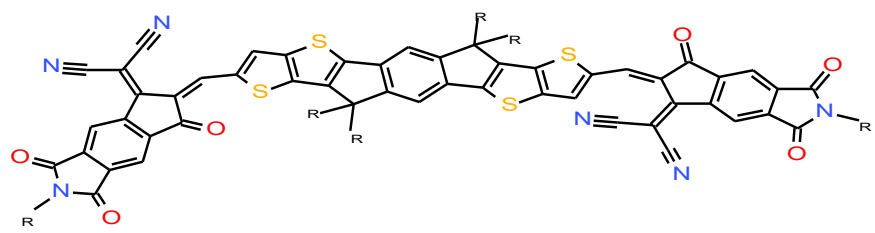
The other approach is with perylene diimide groups for example: In this case the PDI replaces DCI.

Li, S., Liu, W., Li, C. Z., Lau, T. K., Lu, X., Shi, M., & Chen, H. (2016). A non-fullerene acceptor with a fully fused backbone for efficient polymer solar cells with a high open-circuit voltage. *Journal of Materials Chemistry A*, 4(39), 14983-14987.

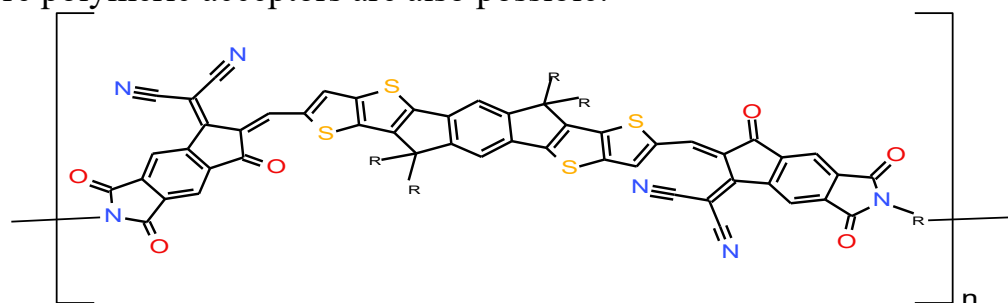
My proposal is to combine DCI with maleimides to produce stronger acceptor groups.



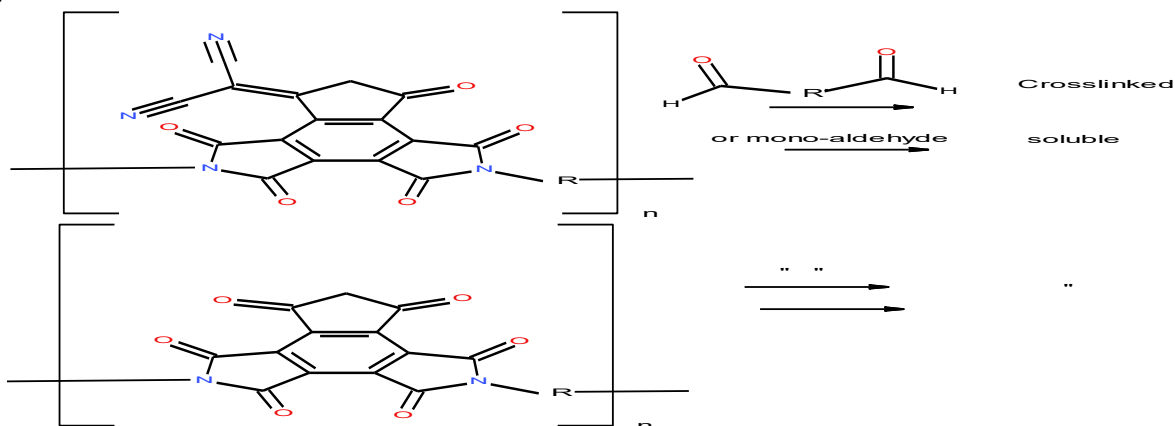
Scheme 7: Examples of combined DCI-PDIs.



Scheme 8: This then would be an example worth considering. Furthermore polymeric acceptors are also possible:

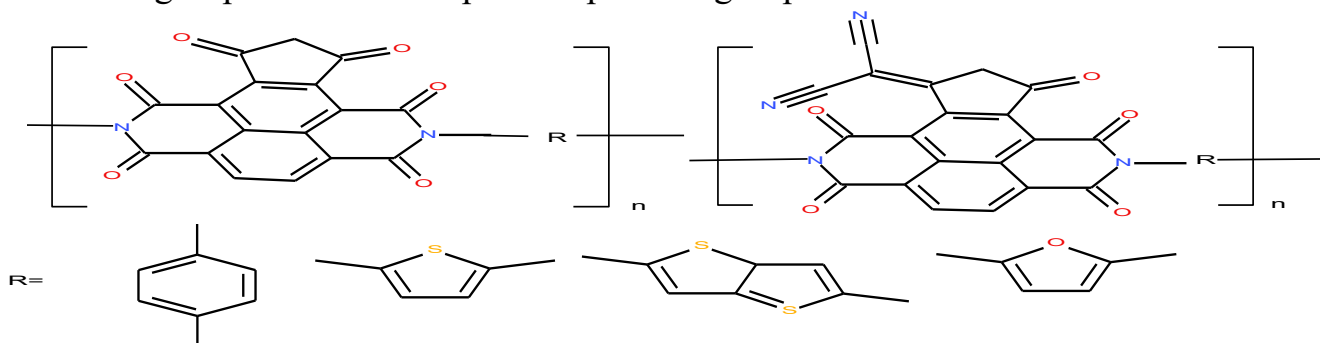


Scheme 9: Example of a polymeric acceptor. If the R backbone groups are also donor structures then the copolymers would be potential candidates for single component solar cells.



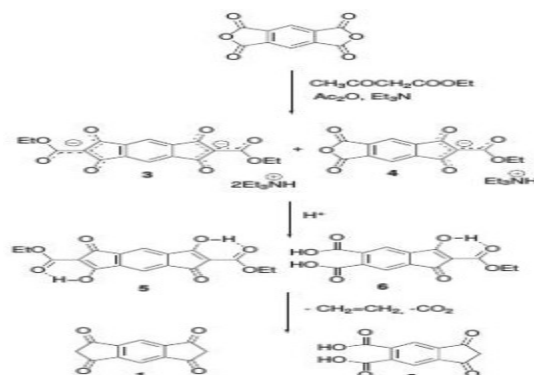
Scheme 10: Polymeric DCI polyamide crosslinked, where the dialdehyde crosslinker can be the same as employed in ITIC type synthesis, for example or a mono-aldehyde version or a donor polymer aldehyde derivative. Which leads me to suggest that this is a

way to synthesize single component solar cells. The donor structures can also be the R backbone groups with the acceptors as pendent groups or vice versa.



Scheme 11: I'm less sure as to the synthesis of these diimides but think it is doable. The resulting polymers can be functionalized with the same reasoning as described in scheme 10 applies here also. The R groups are just suggestions, see scheme 10 for other possibilities.

Synthesis:



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-indanedione: Old and New 1, 3-Indandione Derivatives. *Synthesis*, 2004(15), 2509-2512.

Unlike the above reference, I would first prepare the mono imide which would protect that moiety during the formation of the dione. Mellitic anhydride can be condensed first to form the diimide and then the dione. I think my approach is straight forward and would afford high yields.

Thank you for reading these proposals.  
Dr. Robert B. Login