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# Decrease the Bandgap of Conjugated Polymers: What is the Effect of Alternating Two Acceptor Units Instead of Donor and Acceptor on Optoelectronic Properties?

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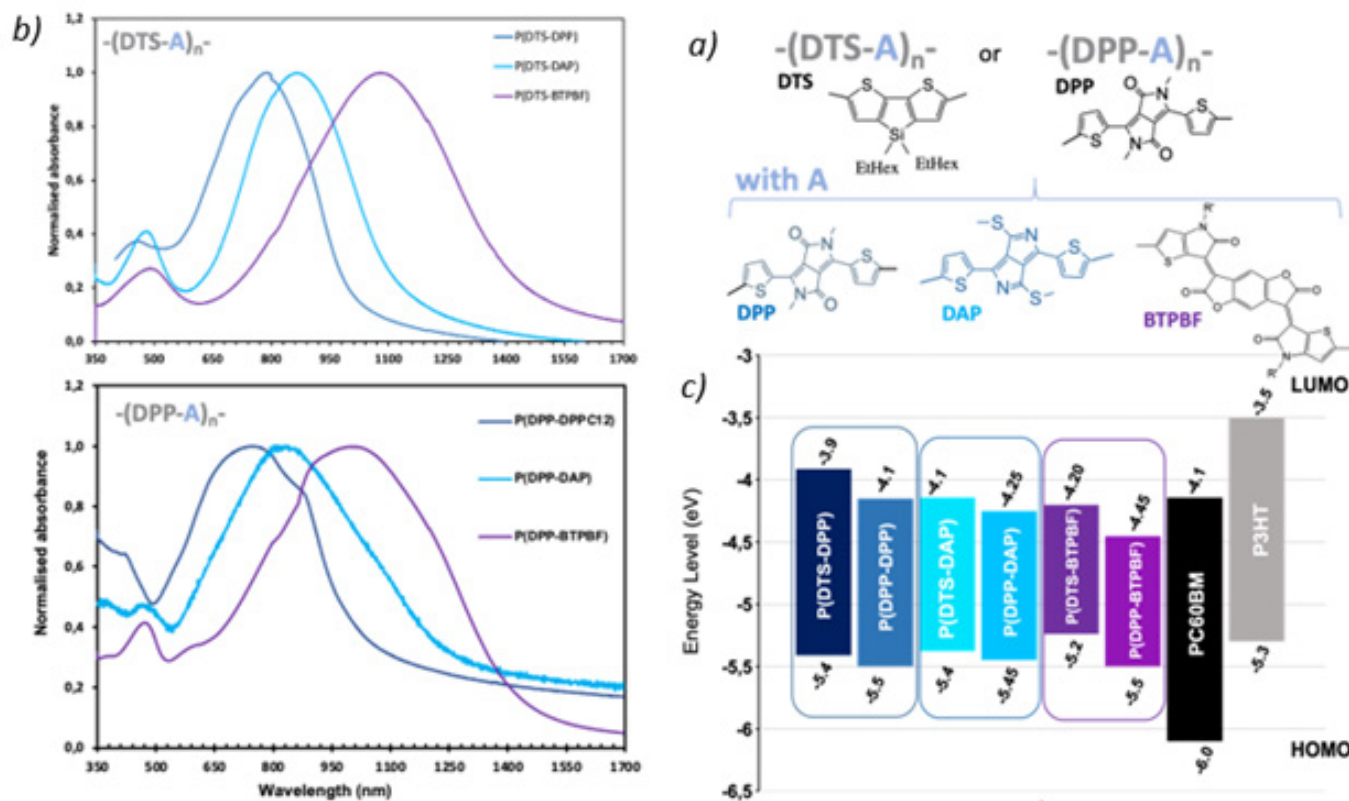
## Opinion

Organic chemistry is a powerful tool to provide highly versatile materials suitable for numerous applications. In the field of organic electronics, there is a high demand of developing materials with particular opto-electronic properties, wide bandgap, low or ultra-narrow bandgap. Different strategies were demonstrated to finely control the bandgap [1]. For organic photovoltaics, photodetectors, biomedical applications, decreasing the optical gap to provide an absorption in the near infrared can be requested. One advantage of macromolecules compared to molecules is that polymers naturally present a decrease of the bandgap by increasing the number of repeating units [2]. However, to strongly shift the absorption range toward the infra-red, the strategy of copolymers alternating electron rich (donor) and electron poor (acceptor) comonomers is one of well-known method leading to donor-acceptor copolymers (D-A) called low bandgap polymers [3]. From our experience based on experimental and computational results, we found that in D-A copolymers, the change of comonomer D based on dithiophene bridged by C, N or Si, while keeping A the same, has little effect on the final opto-electronic properties [4]. Indeed, roughly the same transition energies were obtained. The greatest tunability can be brought by the variation of the acceptor comonomer A. The investigation of D-A copolymers with different A showed that the HOMO levels are similar, only LUMO levels are deepened, provoking the bandgap decrease. This is of particular interest for organic photovoltaic applications as it is more suitable to keep the HOMO level deep, in order to ensure an optimised open circuit voltage which originates from the energy difference between the HOMO of D and the LUMO of A [5]. Pursuing the aim to further decrease the bandgap, the question of the impact of alternating two different electron poor units in a copolymer, instead of D-A was considered. Therefore, A-A copolymers analogous to the previous D-A copolymers were considered [6].

In this comparison, D-A copolymers were based on Dithienosilole (DTS) donor accepting unit combined with three different strong acceptor A units: DPP, DAP and BTPBF (see Figure 1a for structures). The choice of these units was motivated by their potential to promote an absorption in the near infra-red, plus the ease of synthesis for DPP, the possibility to derivate synthesis of DAP from DPP [7] and finally BTPBF for its known strong electron accepting strength [8]. For the series of A-A copolymers, the same A units were considered combined with DPP comonomer (A) instead of DTS (D) [6]. Surprisingly, the analogous copolymers either prepared with DTS (D-A) or DPP (A-A) had approximately the same absorption range (see spectra of thin films in Figure 1b) and in particular similar optical bandgap. Further investigation by cyclic voltammetry to determine oxidation/reduction potentials, gave insights of how HOMO and LUMO energy levels are positioned. Figure 1c shows that when switching from D-A to A-A, electrochemical gaps are also maintained, but both HOMO and LUMO

levels are lowered. This effect can be tuned by the strength of the acceptor unit (in the present example with BTPBF). In conclusion, switching from D-A to A-A copolymers has no significant effect on the bandgap, but allows to more or less deepen both HOMO and

LUMO levels, depending on the acceptor strength of the A unit. This strategy opens the way to a large variety of materials weakly sensitive to oxidation and with optoelectronic properties that could be adapted to the needs.



**Figure 1:** a) chemical structures of compared D-A and A-A copolymer; b) UV-visible-NIR absorption spectra of thin films; c) electronic levels determined from cyclic voltametry.

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