Towards conjugated polymers with low exciton binding energy
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6.1 On the search for the exciton binding energy-structure relationship of conjugated polymers

By and large, the study presented in this thesis has made two establishments: (1) In a donor-acceptor cross-conjugated polymer with thieno[2,3-c]pyrrole-4,6-dione as the acceptor, the hole-electron distance is probably not increased relative to the linear-conjugated case. Hence, a decreased exciton binding energy was not observed (contrary to intuition). (2) Theoretically, electronically effective and spatially small acceptor moieties as the pendant groups do not decrease exciton binding energies relative to their respective linear-conjugated counterparts. These observations contribute to the principles of designing low $E_b$ polymers. They have inspired us to derive reasonable hints to the proper design of the next-phase polymers with low exciton binding energies. Below, we briefly discuss these inspirations with two perspectives.

(i) We learn forthwith from Chapter 5 that to attain a reduced $E_b$, the conjugated system should be sufficiently capable to delocalize the charge (the electron, in our case), rather than to localize it. In spite of the extremely limited number of reports on the relationship between $E_b$ and chemical structures, it is worth noting that a few reports have highlighted the contribution of extensive charge delocalization to efficient charge generation in polymer:fullerene blends.\textsuperscript{1,2,3,4} In this context, we propose that simply considering the influence of conjugation length of donor moieties (i.e. the delocalization of the excitonic hole) in conjugated polymers on their exciton binding energy characteristics may be interesting. To do this, we constructed three linear-conjugated dimer structures in series and subjected them to quantum chemical calculations. The structures are shown in Figure 1.
Figure 1. Structures of three calculated dimer structures with increasing thiophene-based conjugation length. These calculations were conducted in a dielectric medium of propanoic acid. Details of the quantum chemical calculations are the same as those of BDT-cross/linear (see Table 1, Chapter 5).

The calculation results\(^5\) indicated that when the number of conjugated thiophene units increased from 2 to 4 (corresponding to structures T2, T3 and T4, respectively), the exciton binding energy sequentially decreased from 0.71 eV for T2, to 0.65 eV for T3, and finally to 0.59 eV for T4. These results nicely point to the possibility to decrease the intrinsic exciton binding energies of conjugated polymers, simply by optimizing the length of continuously conjugated donor (or acceptor) moieties. Certainly, in designing actual polymers, it is paramount to seek a balance between the conjugation length of donor moieties and other molecular/material properties, such as the optical bandgap, regio-regularity, steric hindrance, solubility, etc.

(ii) Another potentially interesting angle to look at the exciton binding energy-structure relationship, regards the physical size of the electron-withdrawing moieties. This perspective, by nature, is precisely the same as discussed in (i), since a spatially bigger conjugated moiety would allow the electron to be delocalized to a larger extent. In this context, the cross-conjugation strategy does not necessarily become void, given the utilization of a properly sized acceptor moiety.

Ubiquitously, preceding investigations on polymer structures had explicit goals of tuning energy levels and morphologies. This has led to a significant understanding on the property dependence on structure. Due to the feasibility of effectively tuning these properties with various small acceptor moieties, spatially sizable acceptors rarely received dedicated attention, with only a couple of examples.\(^6,7\) With the appreciation for the unique possibility where donor-acceptor cross conjugation reduces the intrinsic exciton binding energy of conjugated polymers, we have conducted a proof-of-concept \(E_b\) evaluation with the help of quantum chemical calculations on the structures shown in Figure 2.
Figure 2. Structures of two calculated dimer structures, featuring differently sized acceptor moieties. CC-sa means cross-conjugation-small-acceptor, and CC-ba means cross-conjugation-big-acceptor. These calculations were conducted in a dielectric medium of propanoic acid. Details of the quantum chemical calculations are the same as those of BDT-cross/linear (see Table 1, Chapter 5).

Despite the difference in the electron-withdrawing capabilities, we focused on the size effect of the acceptors in cross-conjugated systems. When positioned in a dielectric medium of propanoic acid, CC-sa was calculated to have an exciton binding energy of 0.73 eV. When a spatially more sizable acceptor was employed, the exciton binding energy of such a dimer structure drastically reduced to 0.45 eV. Although we do not provide a detailed analysis on the electronic structures of these molecular structures, as we did in Chapter 5, this contrasting result seems to indicate that there is spacious room to play in for the exploration of the potential of cross-conjugated donor-acceptor systems.

Looking back upon the path we have been on, we have confirmed, based on several evidences, that charge delocalization, rather than localization, most likely constitutes one of the fundamental principles for the design of conjugated polymers with intrinsically low exciton binding energies. Finally, we hope for a proper utilization of the donor-acceptor cross-conjugation principle in more rational, systematic, and productive future studies.
6.2 References

5 Unpublished data.