Molecular Design of Small-Bandgap Organic Semiconductors Incorporating Fused Heterocyclic Quinoids

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Small-bandgap organic semiconductors are attractive optoelectronic materials due to their optical absorption and emission in the near-infrared (NIR) region as well as their ambipolar carrier transport properties. In particular, materials with a small bandgap of less than 1.1 eV (corresponding to a wavelength of 1100 nm) could be a promising alternative to silicon. To develop such small-bandgap organic semiconductors, a donor-acceptor (D-A) approach is effective for reducing the bandgaps; however, raising the HOMO level often compromises air stability during carrier transport. Therefore, lowering the LUMO level by incorporating highly electron-deficient acceptor units is import for the development of small-bandgap materials.

To this end, we have explored a series of fused heterocyclic quinoids having two key structural features, i) proaromatic benzo- and naphtho-quinodimethane substructures and ii) electron-withdrawing carbonyl termini, both of which can stabilize the anionic state of the skeleton thus resulting in the highly electron-deficient nature. Further structural modification of heteroatoms, conjugation length, and the shape/symmetry are also important for fine-tuning the electronic structures of the quinoidal skeletons. We systematically incorporated the quinoidal skeletons into D-A oligomers and polymers and investigated structure-property relationships of their optical and electronic properties as well as carrier transport properties for rational molecular design of small-bandgap organic semiconductors (Fig. 1).

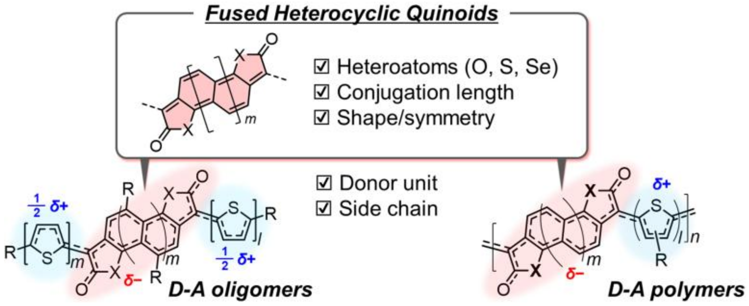
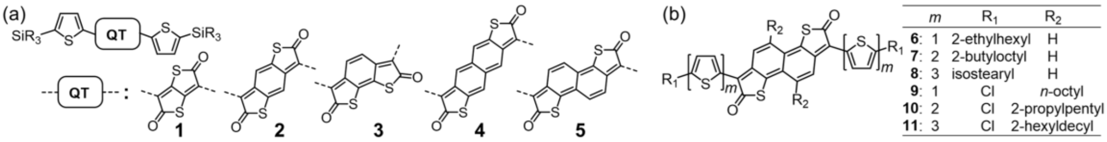


Fig. 1. Molecular design of D-A semiconducting oligomers and polymers in this work.

Our initial study focused on dithienyl D-A-D triads incorporating a series of thienoquinoids **1**–**5** (Fig. 2a). With the π-extension of the quinoidal structures from **1**, the triads **2**–**5** exhibited significantly low-lying LUMO energy levels (−4.2 to −4.3 eV) as well as absorption in the visible to NIR region. These results indicated the highly electron-deficient nature of the quinoidal skeletons, particularly the naphthodithiophenedione skeletons. Then, one of the naphthodithiophenediones was flanked with extended oligothiophene donors for further reducing the bandgap (Fig. 2b). With the extension of the donor units, the absorption maxima of **6**–**8** in solution were increased from 690 to 834, and to 903 nm, all of which, however, were blue-shifted in thin films. In sharp contrast, **9**–**11** with the same D-A-D backbone as **6**–**8** but with solubilizing substituents at the quinoidal core instead of the flanking donor units exhibited significant red-shifts of their absorption bands from the solution to the thin-film state. Single-crystal X-ray analyses revealed that the position of the solubilizing substituents critically affects the intermolecular arrangement of the transition electric dipole moment, where the end- and core-alkylated triads form side-by-side (H-aggregation) and slip-stacked (J-aggregation) arrangements, respectively.

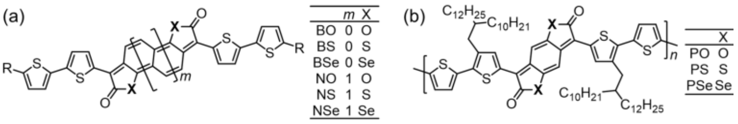


	m	R_1	R_2
6:	1	2-ethylhexyl	H
7:	2	2-butyloctyl	H
8:	3	isostearyl	H
9:	1	Cl	*n*-octyl
10:	2	Cl	2-propylpentyl
11:	3	Cl	2-hexyldecyl

Fig. 2. Thienoquinoid-based D-A-D triads.

Another series of D-A-D triads based on the fused heterocyclic quinoids with oxygen and selenium atoms instead of sulfur atoms were also investigated (BXs and NXs in Fig. 3a). Regardless of the chalcogen atom, the quinoidal structures are highly electron-deficient. Thus, all BXs and NXs showed small bandgaps with low-lying frontier orbital energy levels, enabling air-stable hole and electron transport. Interestingly, the oxygen analogs BO and NO showed one-order-of-magnitude higher mobilities than those of the sulfur and selenium analogs. Single-crystal X-ray analyses indicate that the smaller sizes of the oxygen atom compared to the sulfur and selenium atoms leads to coplanar and rigid backbones, thus suppressing structural and energetic disorder in the solid-state structures, which results in enhanced carrier mobilities. Furthermore, by extending BXs into polymeric systems PXs (Fig. 3b), marked reduction of the optical bandgap to as low as 0.88 eV and significant improvements in the carrier mobilities of up to 2 cm^2 V^{-1} s^{-1} were achieved, where the striking chalcogen-atom-dependance on the mobility was preserved.

These results highlight the great potential of acenedichalcogenophenediones as building units for small-bandgap organic semiconductors. In the presentation, detailed structure-property relationships for rational molecular design will be discussed.



	m	X
BO	0	O
BS	0	S
BSe	0	Se
NO	1	O
NS	1	S
NSe	1	Se

	X
PO	O
PS	S
PSe	Se

Fig. 3. Acenedichalcogenophenedione-based oligomers and polymers.

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