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Electronic Supplementary Information

Doping mechanisms of N-DMBI-H for organic thermoelectrics: hydrogen removal vs hydride transfer†

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Computational methods

To choose a reliable method for describing the enthalpy changes of N-DMBI-H to release a neutral hydrogen atom or hydride anion, we compared the calculated results obtained by different computational schemes with the available experimental data in acetonitrile at room temperature, as shown in Table S1. It is found that the DFT-M062x/6-31g(d,p) method in combination with the polarizable continuum model (PCM) can provide a reliable description of the enthalpy changes for both the hydrogen and hydride release reactions. So the DFT-M062X/6-31g(d,p) + PCM method was chosen for the optimizations of geometric structures and calculations of the total energies and the enthalpy changes in our work. To consider weak intermolecular interactions, the Grimme's D3 dispersion correction was also included in the calculations for the complexes and dimers of the semiconductors. All the optimized structures were confirmed be a real energy minimum with no imaginary vibration frequency by frequency analyses at the same computational levels as the geometry optimizations. In addition, to obtain a better description, the electronic-structure properties and the charge transfer amounts were calculated based on the optimized geometries by using the long-range corrected functional ωB97X with the range separation parameter ω optimally determined according to the gap-tuning procedure. All these calculations were performed by using the Gaussian 16 program package.

Table S1. Experimental and DFT-calculated enthalpy changes (in kcal/mol) of N-DMBI-H to release a neutral hydrogen atom ($^{\Delta H}_{H^{\bullet}}$) or hydride anion ($^{\Delta H}_{H^{-}}$) in acetonitrile at room temperature (method A//method B: geometry optimizations and frequency calculations were performed by using the A method, and then based on the optimized geometries, single-point energy calculations were performed by using the B method).

	$\Delta H_{H^{\bullet}}$	$\Delta H_{H^{-}}$
exp.	75.1	50.6
B3LYP/6-31g(d,p)//B3LYP/6-31g(d,p)	77.2	38.7
B3LYP/6-31g(d,p)//B3LYP/6-311++g(2df,2p)	75.7	30.0
M06-2X/6-31g(d,p)// M06-2X/6-31g(d,p)	80.3	47.8
M06-2X/6-31g(d,p)//M06-2X/6-311++g(2df,2p)	78.9	38.8

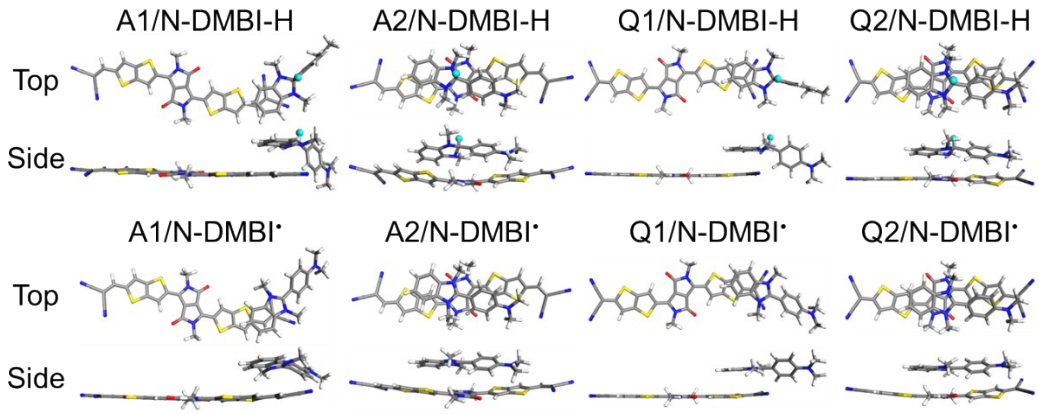

Fig. S1 Optimized geometries of complexes A1, A2, Q1 and Q2 before and after removal of hydrogen atom.

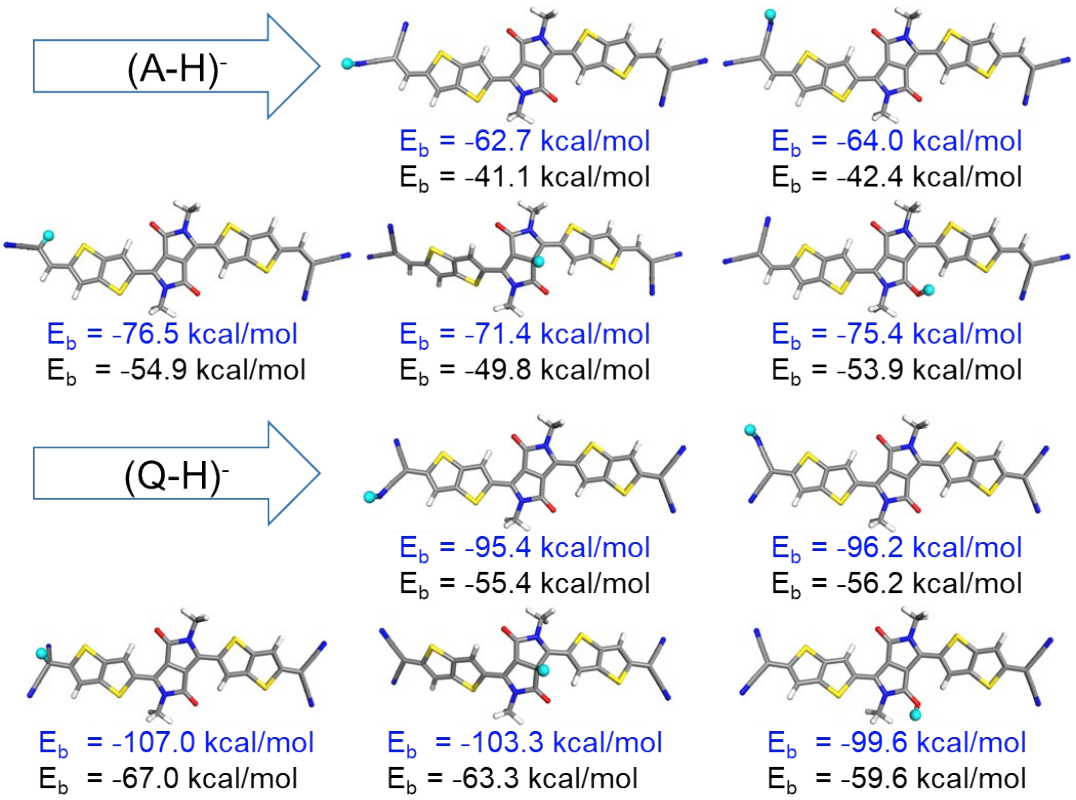

Fig. S2 Optimized geometries and binding energies (in kcal/mol) for the adsorption of hydride on the semiconductors (blue: binding energies of anionic H^- on neutral semiconductors; black: binding energies of radical $H^\bullet$ on anionic semiconductors).

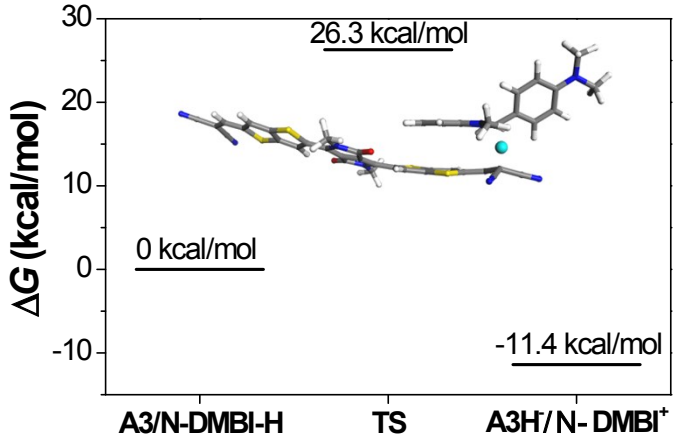

Fig. S3 Gibbs free energies of the hydride transfer reaction in the N-DMBI-H doped A-DCV-DPPTT (Inset: optimized geometry of the transition state).

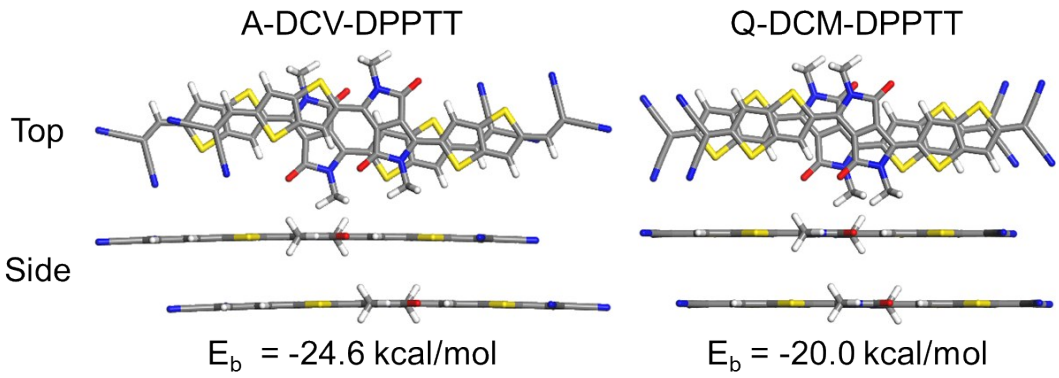

Fig. S4 Optimized geometries and binding energies for the π-π stacking dimers of A-DCV-DPPTT and Q-DCM-DPPTT.