Supporting information

1. Computational methods of electronic coupling

The intermolecular effective charge transfer integral V_{ij} can be calculated directly by

$$V_{ij} = \left| \frac{J_{ij} - S_{ij}(e_i + e_j)/2}{1 - S_{ij}^2} \right| \tag{S1}$$

where charge-transfer integrals (J_{ij}), the site energies (e_i,e_j), and spatial overlap (S_{ij}) can be calculated from

$$e_i = \langle \psi_i | H | \psi_i \rangle \tag{S2}$$

$$e_j = \langle \psi_j | H | \psi_j \rangle \tag{S3}$$

$$J_{ij} = \langle \psi_i | H | \psi_j \rangle \tag{S4}$$

$$S_{ij} = \langle \psi_i | \psi_j \rangle \tag{S5}$$

2. Computational methods of reorganization energies based on AP method

According to the AP method, the λ_i calculation formulae for one molecule can be written with as following equation:

$$\lambda = \lambda_i = \lambda_r^1 + \lambda_r^2 = [E^0(G^\pm) - E^0(G^0)] + [E^\pm(G^0) - E^\pm(G^\pm)] \tag{S6}$$

λ_r^1 corresponds to the relaxation energy from the stable geometry of the ionic state to the lowest energy geometry of neutral state, and λ_r^2 corresponds to the relaxation energy of the reverse process.

The λ_i calculation formulae for two different molecules (A and B) can be written with as following equation

$$\lambda = [E_A^0(G^\pm) - E_A^0(G^0)] + [E_B^\pm(G^0) - E_B^\pm(G^\pm)] \tag{S7}$$

The adiabatic ionization potential (*IP*) and electron affinities (*EA*) energies can be computed by the following equations

$$IP = E^+(G^+) - E^0(G^0) \tag{S8}$$

$$EA = E^-(G^-) - E^0(G^0) \tag{S9}$$

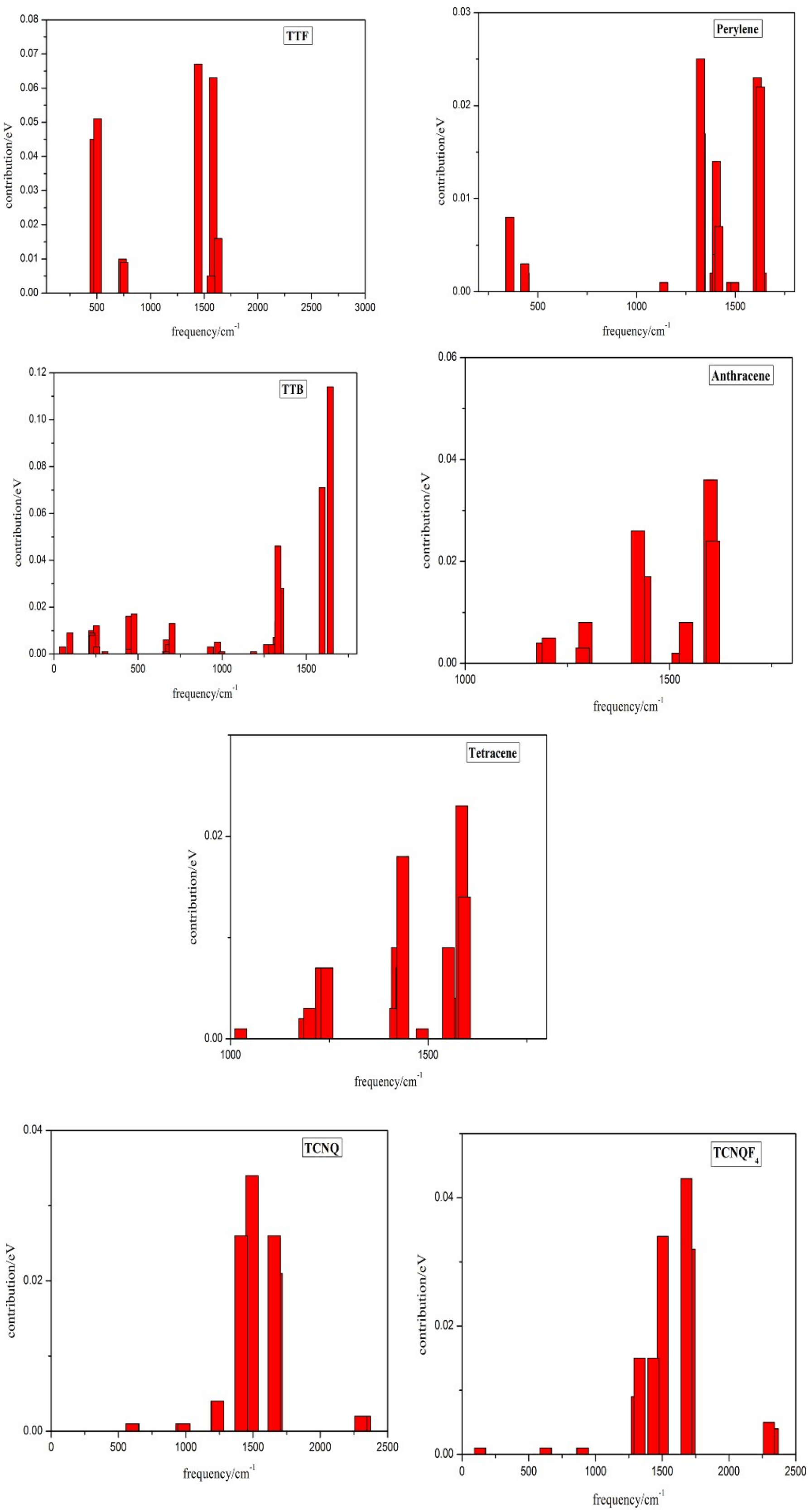

Fig. S1. Contributions of each vibrational mode to the hole reorganization energies for all molecules.

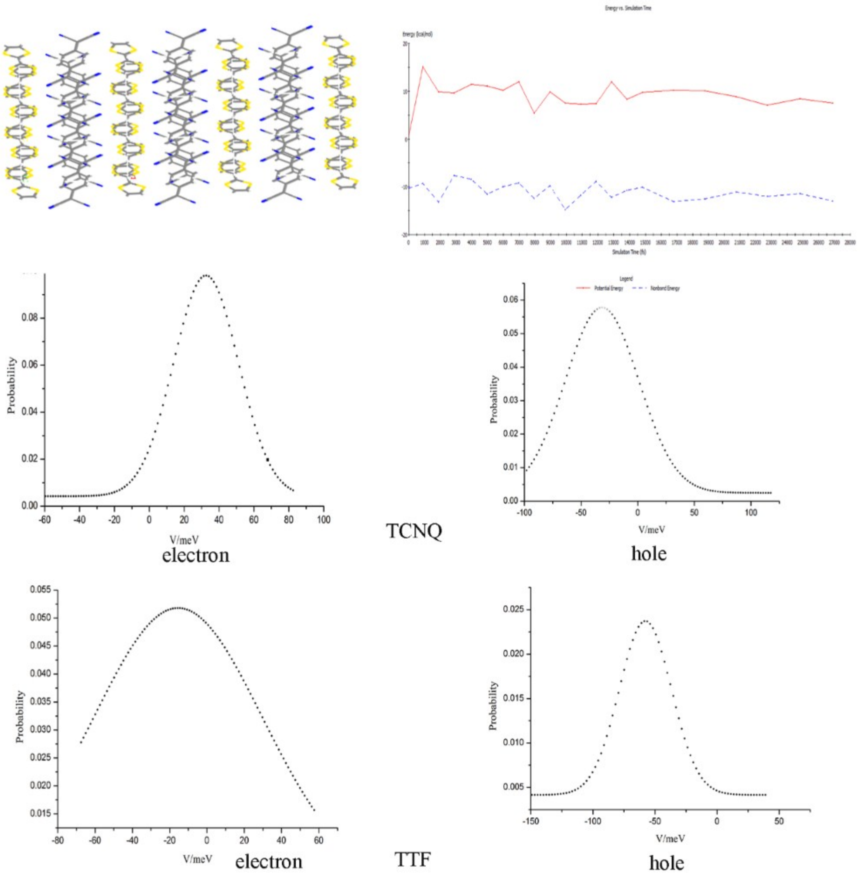

Fig. S2. Gaussion fitting of the transfer integrals (in meV) for the major hopping pathway for TTF and TCNQ with sampling time at 300K.