Strategy to improve the efficiency of hole transporting materials: introduction of

highly symmetrical core

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Computational details

Molecular stable dimers are obtained through two steps. Firstly, MD of 30 ps simulation are carried out at 298K in the NVE ensemble with a time step of 1 fs by using the DFTB+ 1.0.1 package to get rough dimeric structures. Secondly, the rough dimers with the lowest energies from dynamics simulation are selected as the starting geometries and optimized to their potential energy minimum at B3LYP/6-31G(d,p) level with Gaussian 09 program package.

The hole mobility of investigated molecules are calculated by using Einstein relation

$$u = \frac{1}{2n} \frac{e}{k_B T} \sum_i r_i^2 k_i P_i$$

where n is the spatial dimensionality and is 1 in our work, i is a selected hopping pathway, r_i represents the charge hopping centroid to centroid distance, and k_i denotes the charge hopping rate.

The charge hopping rate (k) is expressed as:

$$k = \frac{4\pi^2}{h} v^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left[-\frac{\lambda}{4k_B T}\right]$$

where k_B is the Boltzmann constant, h denotes the Planck constant, *and T* represents the temperature in Kelvin. The λ represents reorganization energy, which is calculated by using the adiabatic potential energy surface method. v is transfer integral, which can be deduced directly from a direct approach at M06-2X/6-31G(d,p) level.

$$v = \langle \Psi_i^{HOMO} | F | \Psi_f^{HOMO} \rangle$$

where Ψ_i^{HOMO} and Ψ_f^{HOMO} represent the HOMOs of isolated molecules 1 and 2. F is the Fock operator for dimer, which can be calculated as:

$$F = SC\varepsilon C^{-1}$$

S denotes the overlap matrix for dimer. The Kohn-Sham orbital C and eigenvalue ε are evaluated by diagonalizing the zeroth-order Fock matrix. P_i is defined as the hopping probability, which can be obtained by:
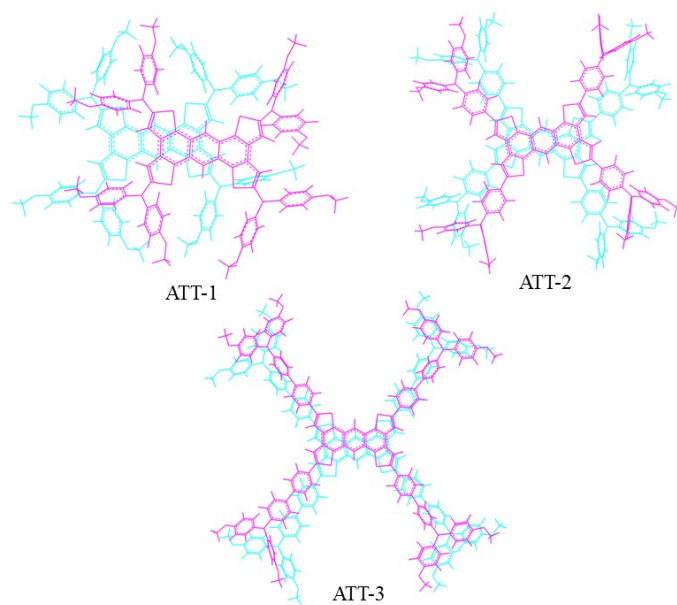
$$P_i = \frac{k_i}{\sum_i k_i}$$

ATT-1

ATT-2

ATT-3

Figure S1. The geometry configurations of stable dimers for ATT derivatives.

Table S1. Hole mobility (calculated value: u_c, cm^{2}v^{-1}s^{-1}; experimental value: u_e, cm^{2}v^{-1}s^{-1}) of Spiro-OMeTAD, HTM1,and OMeTAD-TPA.

Compounds	u_c	u_e
Spiro-OMeTAD	5.56x10^{-3}	1.30x10^{-3}
HTM1	1.33x10^{-6}	6.0x10^{-6}
OMeTAD-TPA	5.75x10^{-4}	1.08x10^{-4}

Table S2. The hole transfer integrals v (eV), the centroid to centroid distances (d, Å), hole hopping rate k (s^{-1}), and hole mobilities (u, cm^{2}v^{-1}s^{-1}) of investigated molecules.

Compounds	v	d	k	μ
att-1	4.2x10^{-2}	4.995	8.08x10^{12}	0.13
att-2	5.71x10^{-2}	2.622	6.17x10^{13}	0.27
att-3	-3.45x10^{-2}	3.949	9.88x10^{12}	0.099

Table S3 Calculated adiabatic ionization potentials (*IP*, eV), adiabatic electron affinity (*EA*, eV), and absolute harnesses (*η,* eV) of investigated molecules.

Compounds	*IP*	*EA*	*η*
Spiro-OMeTAD	4.38	1.14	1.62
ATT-1	4.41	1.94	1.24
ATT-2	4.60	2.10	1.25
ATT-3	4.67	2.21	1.23