

How to regulate energy levels and hole mobility of hole-transporting materials in perovskite solar cells

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Table S1 The HOMO levels (eV) of 30 molecules and mean difference.

Compounds	HOMO ^a	HOMO ^b	HOMO ^c	HOMO ^d	HOMO ^e	HOMO ^f	HOMO ^g	HOMO ^h
HTM ₁	-4.77	-5.04	-5.13	-5.33	-5.48	-5.68	-5.64	-5.36
HTM ₂	-4.66	-4.93	-5.03	-5.23	-5.38	-5.59	-5.56	-5.26
H112	-4.55	-4.83	-4.93	-5.13	-5.28	-5.49	-5.46	-5.29
KTM3	-4.52	-4.83	-4.93	-5.13	-5.28	-5.50	-5.47	-5.13
FA-MeOPh	-4.65	-4.93	-5.02	-5.21	-5.39	-5.56	-5.51	-5.15
TPA-MeOPh	-4.75	-5.02	-5.12	-5.32	-5.47	-5.67	-5.63	-5.29
Py-A	-4.75	-5.02	-5.13	-5.33	-5.49	-5.71	-5.69	-5.41
Py-B	-4.56	-4.83	-4.94	-5.14	-5.29	-5.50	-5.46	-5.25
Py-C	-4.52	-4.79	-4.89	-5.09	-5.23	-5.44	-5.40	-5.11
TPBS	-4.68	-4.95	-5.05	-5.25	-5.40	-5.61	-5.58	-5.30
TPBC	-4.67	-4.95	-5.04	-5.24	-5.39	-5.59	-5.55	-5.33
DMFA-TPA	-4.65	-4.92	-5.02	-5.21	-5.36	-5.57	-5.52	-5.25
DMFA-FA	-4.60	-4.88	-4.97	-5.17	-5.31	-5.52	-5.46	-5.21
OMeTPA-FA	-4.50	-4.77	-4.87	-5.07	-5.22	-5.44	-5.40	-5.14
OMeTPA-TPA	-4.54	-4.81	-4.92	-5.12	-5.27	-5.49	-5.44	-5.13
MeO-TPD	-4.57	-4.84	-5.95	-5.16	-5.31	-5.54	-5.53	-5.10
Spiro-OMeTAD	-4.48	-4.75	-4.86	-5.06	-5.22	-5.44	-5.42	-5.15
Spiro-MeO-TPD	-4.50	-4.77	-4.88	-5.08	-5.23	-5.45	-5.53	-5.10
BPAPF	-4.97	-5.26	-5.36	-5.57	-5.72	-5.94	-5.90	-5.60
Spiro-TTB	-4.66	-4.93	-5.03	-5.23	-5.38	-5.59	-5.56	-5.30
Spiro-TAD	-4.79	-5.07	-5.17	-5.37	-5.52	-5.73	-5.70	-5.40
HTM-1	-4.44	-4.72	-4.83	-5.03	-5.18	-5.40	-5.38	-4.95
HTM-2	-4.49	-4.76	-4.88	-5.08	-5.23	-5.45	-5.43	-5.08
HTM-3	-4.46	-4.73	-4.84	-5.04	-5.20	-5.42	-5.40	-5.02
H101	-4.46	-4.73	-4.83	-5.03	-5.19	-5.41	-5.38	-5.16
BBMPHDPH2	-4.54	-4.82	-4.92	-5.11	-5.27	-5.48	-5.45	-5.33
DPBTD-BBMPDP2	-4.59	-4.86	-4.97	-5.17	-5.32	-5.54	-5.51	-5.34
DPEDOT-BBMPDP2	-4.50	-4.77	-4.87	-5.08	-5.22	-5.43	-5.40	-5.22
CBP	-5.42	-5.72	-5.81	-6.03	-6.19	-6.41	-6.37	-6.23
TPD	-4.80	-5.07	-5.18	-5.38	-5.53	-5.76	-5.73	-5.30
Difference	0.63	0.35	0.22	0.05	-0.10	-0.32	-0.29	/

^a from B3LYP functional;

^b from PBE1PBE functional;

^c from MPW1B95 functional; the iop(3/76=0690003100) should be added in control line of Gaussian calculation.

^d from PBE33 functional; the iop(3/76=1000003333) and iop(3/77=0666706667) should be added in control line of Gaussian calculation..

^e from PBE38 functional; the iop(3/76=1000003750) and iop(3/77=0625006250) should be added in control line of Gaussian calculation..

^f from MPW1K functional; the iop(3/76=0572004280) should be added in control line of

Gaussian calculation..

^g from BHHLYP functional;

^h from experimental values.

Table S2 The calculated HOMO levels (eV) and LUMO levels (eV) of spiro-CPDT analogues.

Compounds	HOMO	LUMO
HTM1	-4.98	-2.62
HTM2	-4.99	-2.63
HTM3	-4.98	-2.49
HTM4	-5.05	-2.75
HTM5	-5.16	-2.74
HTM6	-5.03	-2.72
HTM7	-5.03	-2.69
HTM8	-4.95	-2.64
HTM9	-5.05	-2.72
HTM10	-4.99	-2.72
HTM11	-5.16	-2.73
HTM12	-4.92	-2.47

Table S3 The calculated excitation energies (eV) of spiro-CPDT analogues.

Compounds	Excitation energies
HTM1	2.36
HTM2	2.36
HTM3	2.49
HTM4	2.30
HTM5	2.42
HTM6	2.31
HTM7	2.34
HTM8	2.31
HTM9	2.33
HTM10	2.27
HTM11	2.43
HTM12	2.45

Part 1. The details of calculating hole mobility are given.

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 r_i represents the charge hopping centroid to centroid distance, n is the spatial dimensionality and is 1 in our work, i is a selected hopping pathway, and k_i denotes the charge hopping rate. P_i is defined as the hopping probability, which can be obtained by:

$$P_i = \frac{k_i}{\sum_i k_i}$$

v denotes transfer integral, which is obtained by adopting a direct approach at M06-2X/6-31G(d,p) level. v can be written as:

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

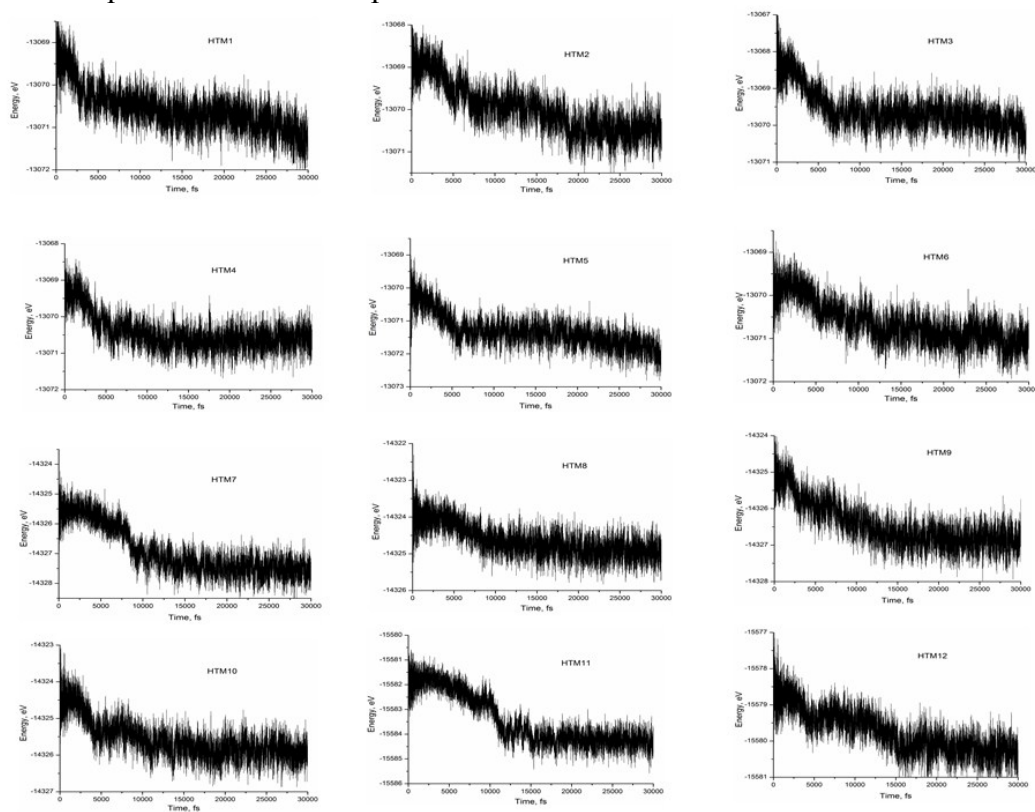
where Ψ_i^{HOMO} and Ψ_f^{HOMO} represent the HOMOs of isolated molecules 1 and 2. F is the Fock operator for dimer, which can be calculated as:

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

S denotes the overlap matrix for dimer. The Kohn-Sham orbital C and eigenvalue ε are evaluated by diagonalizing the zeroth-order Fock matrix.

Part 2. Details about obtaining stable dimers are given.

Molecular stable dimers are obtained through two steps. At first, to get initial dimeric structures, MD of 30 ps simulation have been carried out at 298K in the NVE ensemble with a time step of 1 fs by using the DFTB+ 1.0.1 package. Secondly, the dimers with the lowest energies from dynamics simulation are selected as the starting geometries and relaxed to their potential energy minimum at B3LYP/6-31G(d,p) level with Gaussian 09 program package. The total electronic energy evolutions of the investigated dimers as a function of simulation time are documented in following Figures. From the Figures, we think that the dimers of investigated molecules reach thermal equilibrium within 30 ps.



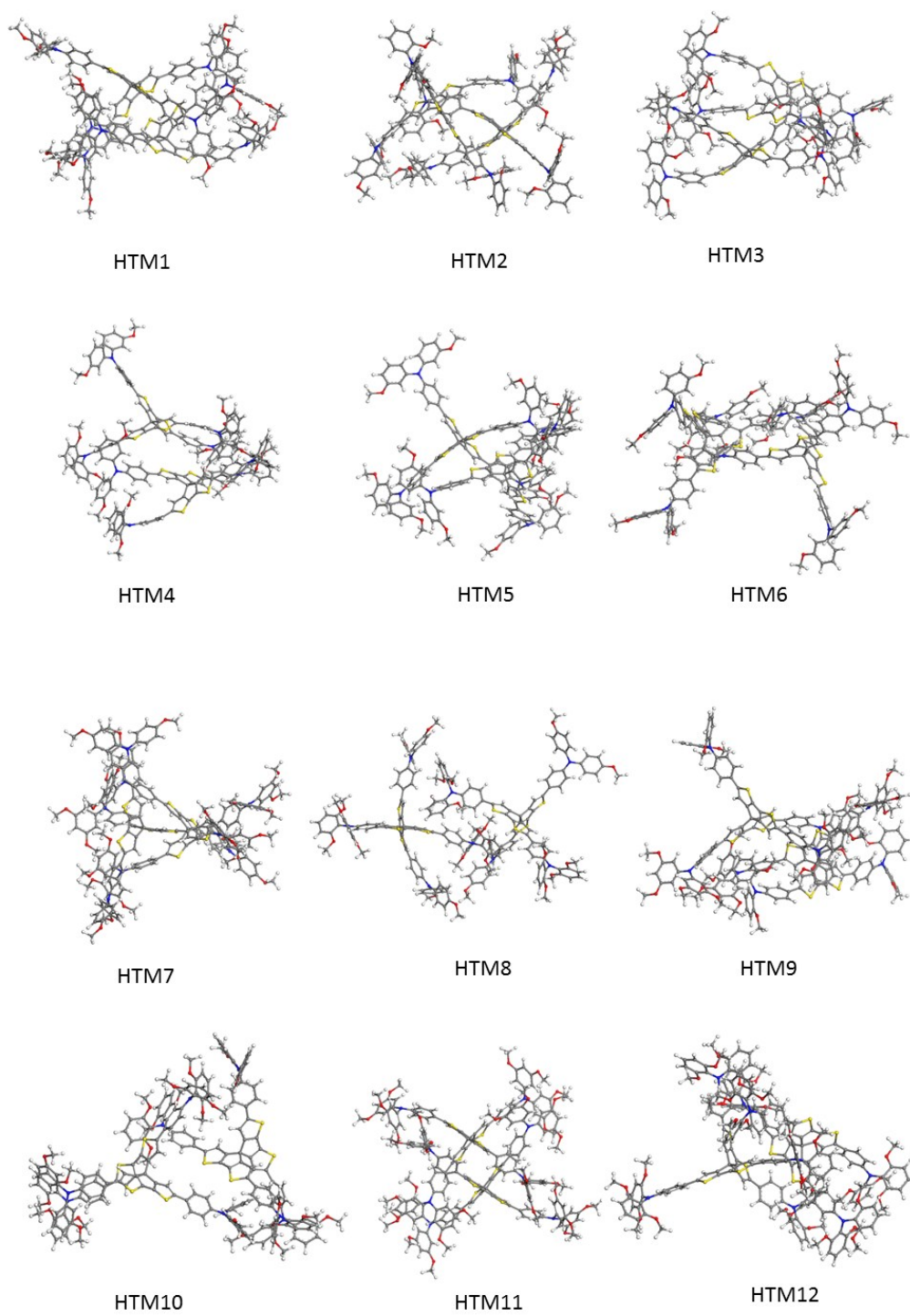


Figure S1. The geometrical configurations of stable dimers.