Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Exploring electrochemical properties of hole transport materials with spiro-core for efficient perovskite solar cells from the first-principles

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Table S1 Calculated HOMO[a] (in eV) and experimental $HOMO_{exp}$ (in eV) of 30 reference molecules and difference between HOMO[a] and $HOMO_{exp}$.

Compounds	HOMO[a]	$HOMO_{exp}$	Difference
HTM_1	-4.77	-5.36	0.60
HTM_2	-4.66	-5.26	0.61
H112	-4.55	-5.29	0.74
KTM3	-4.52	-5.13	0.61
FA-MeOPh	-4.65	-5.15	0.50
TPA-MeOPh	-4.75	-5.29	0.54
Py-A	-4.75	-5.41	0.66
Py-B	-4.56	-5.25	0.69
Py-C	-4.52	-5.11	0.59
TPBS	-4.68	-5.30	0.68
TPBC	-4.67	-5.33	0.66
DMFA-TPA	-4.65	-5.25	0.60
DMFA-FA	-4.60	-5.21	0.61
OMeTPA-FA	-4.50	-5.14	0.64
OMeTPA-TPA	-4.54	-5.13	0.59
MeO-TPD	-4.57	-5.10	0.53
Spiro-MeO-TPD	-4.50	-5.10	0.60
BPAPF	-4.97	-5.60	0.63
Spiro-TTB	-4.66	-5.30	0.64
Spiro-TAD	-4.79	-5.40	0.61
HTM-1	-4.44	-4.95	0.51
HTM-2	-4.49	-5.08	0.59
HTM-3	-4.46	-5.02	0.56
H101	-4.46	-5.16	0.70
BBMPHDPH2	-4.54	-5.33	0.79
DPBTD-BBMPDP2	-4.59	-5.34	0.75
DPEDOT-BBMPDP2	-4.50	-5.22	0.72
CBP	-5.42	-6.23	0.81
TPD	-4.80	-5.30	0.50
1	-4.44	-5.00	0.56

Table S2. Fitting HOMO levels (in eV) of 10 molecules.

Compounds	HOMO[a]	HOMO[b]	$HOMO_{exp}$
T101	-4.61	-5.23	-5.29
T102	-4.73	-5.36	-5.35
T103	-4.70	-5.33	-5.33
Spiro-OMeTAD	-4.48	-5.09	-5.07
apv-EC	-4.71	-5.34	-5.28
apv-T	-4.80	-5.44	-5.31
EtheneDTPA	-4.49	-5.10	-5.19
F101	-4.49	-5.10	-5.18
EtheneTTPA	-4.39	-4.99	-5.02
EDOT-OMeTPA	-4.66	-5.29	-5.28
Mean error	0.624	0.003	

Mean error = $\sum$(HOMO[a]- $HOMO_{exp}$)/10 or $\sum$（HOMO[b]- $HOMO_{exp}$)/10

Table S3. The total electron energy and transfer integral of 4 pathways of Spiro-OMeTAD.

Pathways	Total electron energy(a.u)	Hole transfer integral(eV)
1	-7895.89929	-1.42×10^{-2}
2	-7895.89731	1.05×10^{-2}
3	-7895.87483	-6.86×10^{-3}
4	-7895.83715	-3.72×10^{-3}

Table S4. The centroid to centroid distances (r_i, Å), the hole transfer integrals v (eV), hole hopping rate k (s^{-1}), and hole mobilities (u, $cm^2v^{-1}s^{-1}$) of Spiro-OMeTAD and OMeTPA-TPA.

Compounds	r_i	v	k	u_{cal}	u_{exp}
Spiro-OMeTAD	11.299	2.23×10^{-3}	6.86×10^{10}	5.65×10^{-3}	4.53×10^{-4}
OMeTPA-TPA	5.718	1.28×10^{-3}	2.73×10^{11}	5.75×10^{-4}	1.08×10^{-4}

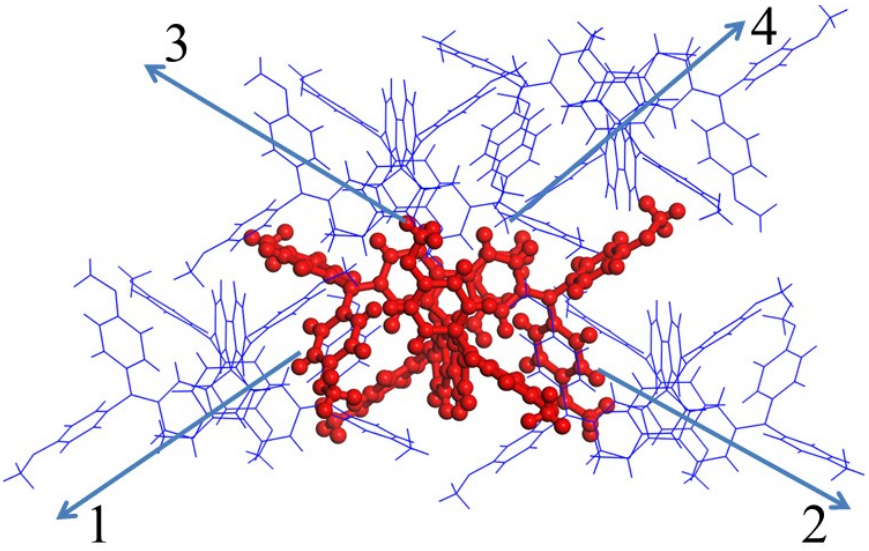

Fig. S1 The hole transfer pathways of Spiro-OMeTAD.

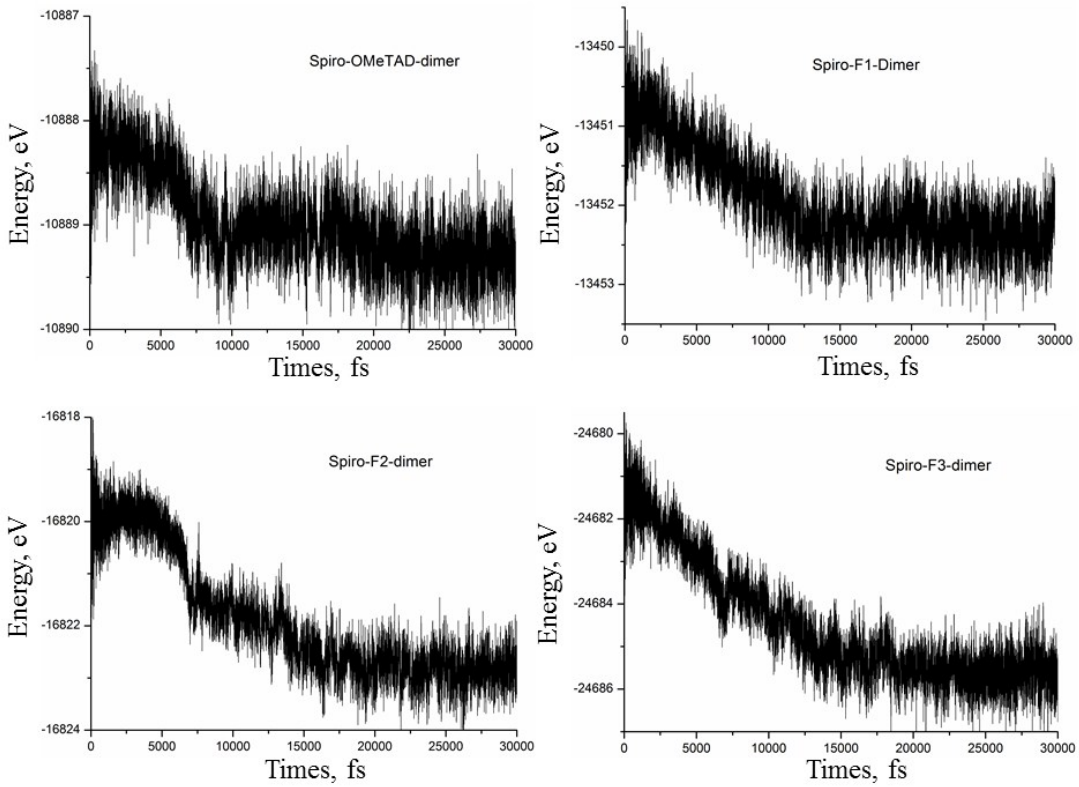

Fig S2. Evolutions of the total electronic energy of the systems as a function of the simulation time.