Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Optimizing electron-rich arylamine derivatives in thiophene-fused as π bridge-based hole transporting materials for perovskite solar cells

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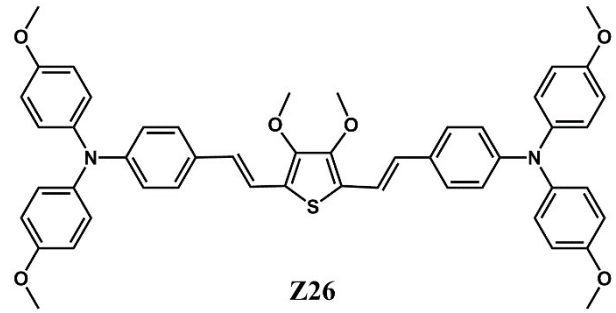


Fig. S1 Chemical structure of the reported hole transporting material Z26.

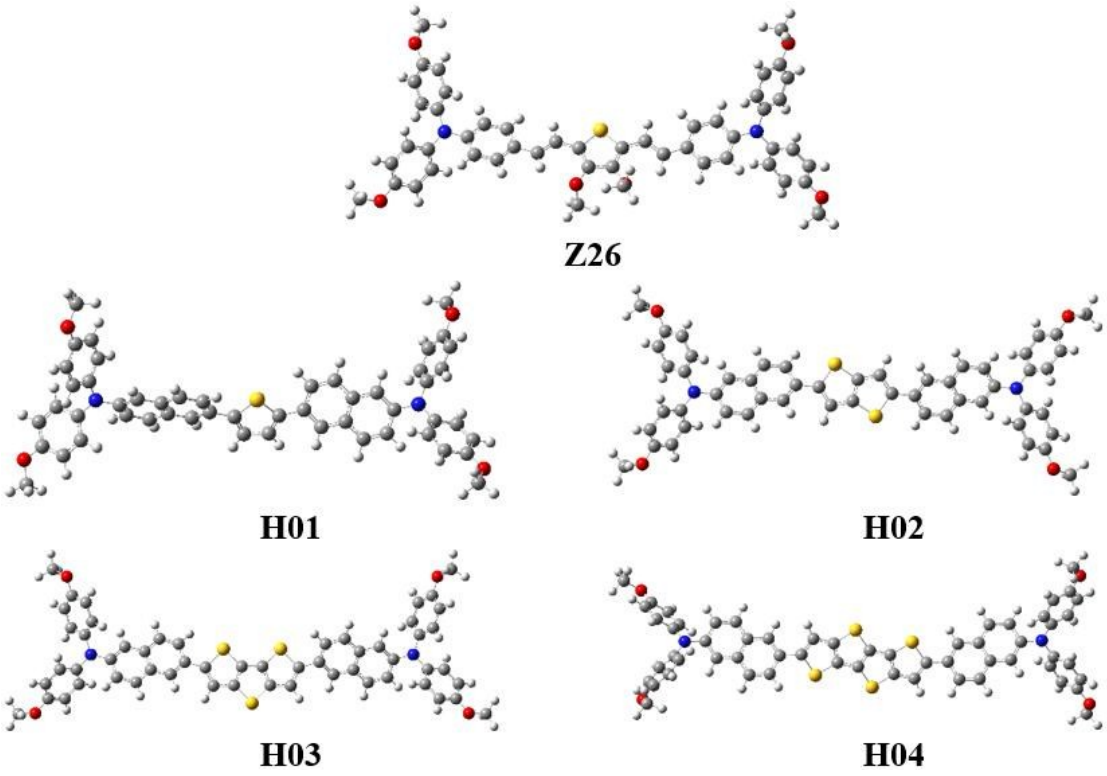


Fig. S2 Optimized structure for the hole transporting materials from B3P86/6-311G(d,p) calculations.

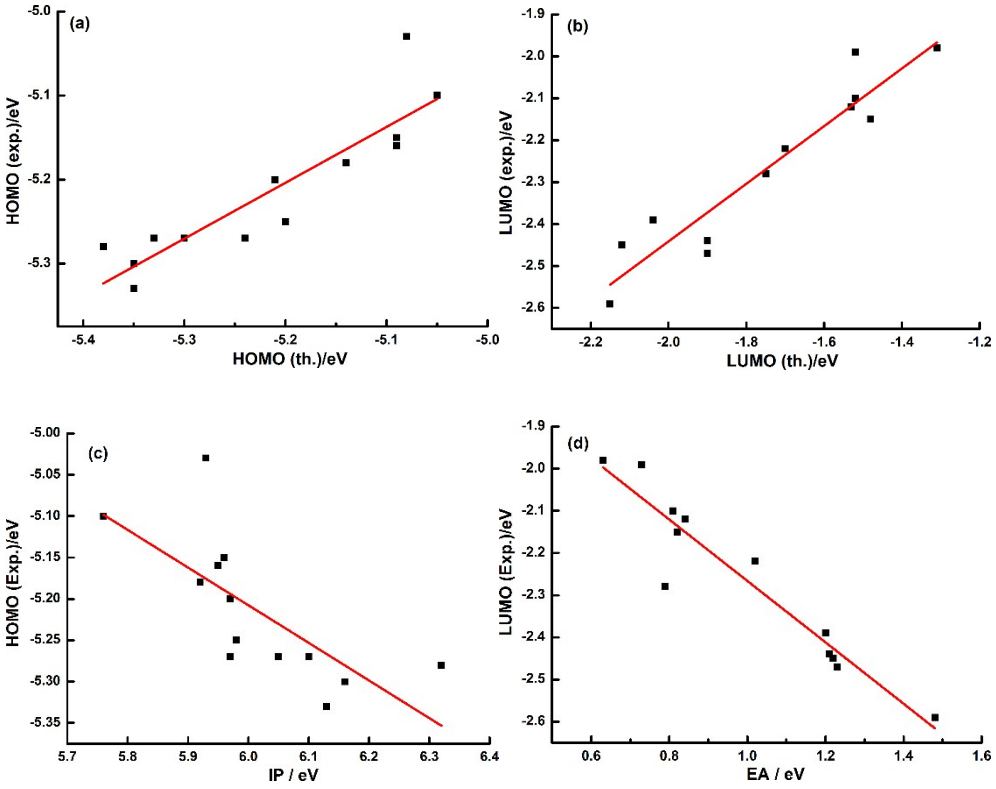


Fig. S3 Linearity of HOMO and LUMO energy between theoretical calculations and experimental data.

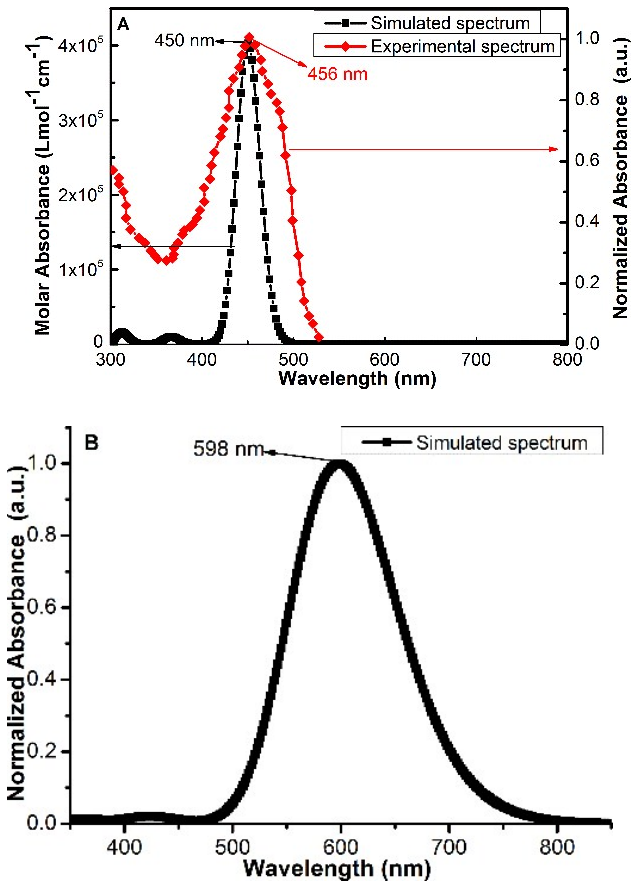
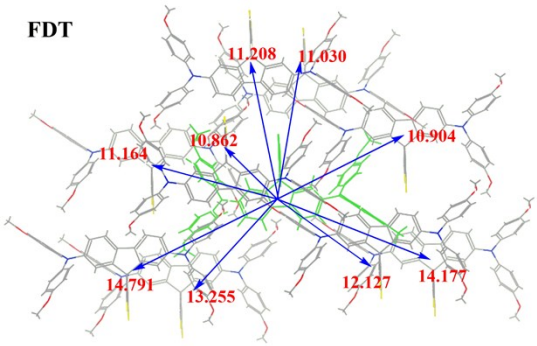
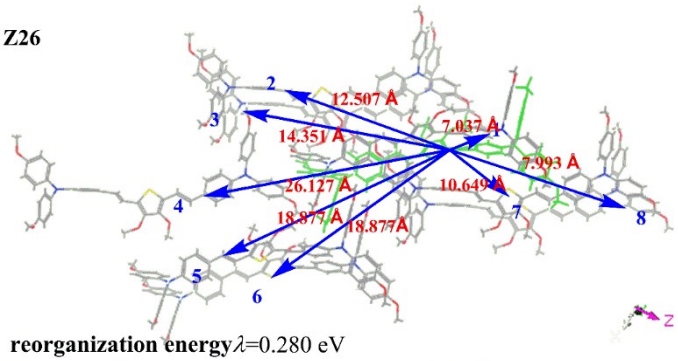


Fig. S4 Simulated absorption spectra (a) and photoluminescence spectra (b) of H1 using the TD-BMK/6-31g(d) functional and basis set in tetrahydrofuran together with the experimental UV-spectra.



reorganization energy λ=0.195 eV

hole transfer integral	hole transport rate	hole mobility
2.728×10^{-4} eV	4.28×10^{8} s^{-1}	2.848×10^{-3} $cm^2V^{-1}s^{-1}$
-2.011×10^{-4} eV	2.32×10^{8} s^{-1}	
-7.533×10^{-4} eV	3.26×10^{9} s^{-1}	
7.402×10^{-4} eV	3.15×10^{9} s^{-1}	
-1.307×10^{-4} eV	9.82×10^{7} s^{-1}	
-9.628×10^{-4} eV	5.33×10^{9} s^{-1}	
-1.530×10^{-3} eV	1.35×10^{10} s^{-1}	
2.171×10^{-3} eV	2.71×10^{10} s^{-1}	
-2.696×10^{-3} eV	4.18×10^{10} s^{-1}	



reorganization energy λ=0.280 eV

hole transfer integral	hole-transport rate	hole mobility
v_1=7.590×10^{-4} eV	k_1 =1.22×10^{9} s^{-1}	u_h =8.05×10^{-4} cm^2 V^{-1} s^{-1}
v_2=4.503×10^{-3} eV	k_2 =4.28×10^{10} s^{-1}	u_{exp}=1.34×10^{-4} cm^2 V^{-1} s^{-1}
v_3=1.933×10^{-4} eV	k_3 =7.88×10^{7} s^{-1}	
v_4=2.805×10^{-3} eV	k_4 =1.66×10^{10} s^{-1}	
v_5=2.271×10^{-4} eV	k_5 =1.09×10^{8} s^{-1}	
v_6=1.045×10^{-3} eV	k_6 =2.30×10^{9} s^{-1}	
v_7=1.701×10^{-3} eV	k_7 =6.10×10^{9} s^{-1}	
v_1=8.233×10^{-3} eV	k_8 =1.43×10^{11} s^{-1}	

Fig. S5 Main hole-hopping pathways and computational parameters (center-of-mass distance *D* highlighted in red color) on basis of crystal structures for Z26 and FDT. Hole mobility of u_{exp} come from the reference[1].

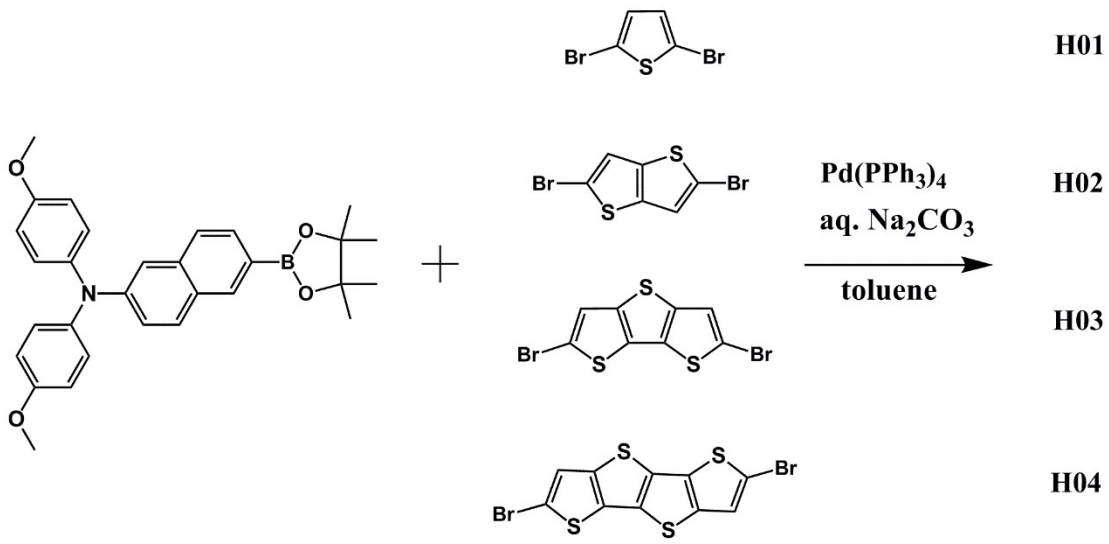


Fig. S6 Recommended synthesis schemes and chemical structures of H01-H04.

Table S1 HOMO and LUMO energy levels of theoretical calculation and experimental values for HTMs.

	IP	EA	HOMO (Exp.)	HOMO(Th.)	LUMO (Exp.)	LUMO(Th.)	Ref.
AS37	5.93	0.73	-5.03	-5.08	-1.99	-1.52	[2]
BTT-1	5.97	0.63	-5.2	-5.21	-1.98	-1.31	[3]
H-Di	6.10	1.02	-5.27	-5.30	-2.22	-1.70	[4]
Z25	5.92	1.21	-5.18	-5.14	-2.44	-1.90	[1]
FDT	5.95	0.79	-5.16	-5.09	-2.28	-1.75	[5]
X59	5.96	0.81	-5.15	-5.09	-2.10	-1.52	[6]
H-Tri	6.05	0.82	-5.27	-5.33	-2.15	-1.48	[4]
spiro-OMeTAD	5.76	0.84	-5.1	-5.05	-2.12	-1.53	[1]
Th101	5.98	1.23	-5.25	-5.20	-2.47	-1.90	[7]
Tth101	5.97	1.48	-5.27	-5.24	-2.59	-2.15	[7]
apv-EC	6.32	1.04	-5.28	-5.38	-	-	[8]
TPBC	6.13	1.20	-5.33	-5.35	-2.39	-2.04	[9]
TPBS	6.16	1.22	-5.3	-5.35	-2.45	-2.12	[9]

Table S2 Calculated HOMO, LUMO, IP and EA together with experimental values for designed HTMs.

	HOMO (th.)[a]	HOMO (exp.)[b]	HOMO (meas.)[c]	LUMO (th.)[a]	LUMO (exp.)[d]	LUMO (meas.)[c]	IP[a]	HOMO (exp.')[e]	EA[a]	LUMO (exp.')[f]
H01	-5.31	-5.25		-2.16	-2.56		6.03	-5.25	1.51	-2.64
H02	-5.31	-5.25		-2.24	-2.62		6.01	-5.24	1.58	-2.69
H03	-5.32	-5.26		-2.34	-2.68		6.00	-5.24	1.67	-2.76
H04	-5.35	-5.28		-2.45	-2.76		6.01	-5.24	1.80	-2.85
Z26	-5.05	-5.08	5.16[h]	-2.35	-2.69	-2.77[h]	5.77	-5.13	1.64	-2.74
FDT	-5.09	-5.11	5.16[i]	-1.75	-2.28	-2.28[i]	5.95	-5.22	0.79	-2.12

[a]from the B3P86/6-311G(d,p) calculations; [b]from $HOMO(\text{exp.})=0.66HOMO(\text{cal.})-1.75$; [c]from cyclic voltammogram measure; [d] from $LUMO(\text{exp.})=0.69LUMO(\text{th.})-1.07$; [e] from $HOMO(\text{exp.}')=-0.46IP-2.48$; [f] from $LUMO(\text{exp.}')=-0.73EA-1.54$; [h]from ref.12; [i]from ref.28.

Table S3 Adiabatic ionization potential (IP_a in eV), electron affinities (EA_a in eV), absolute hardness (η in eV), exciton binding energy (E_b in eV), and solvation free energy (ΔG in eV) of molecules Z26.

	IP_a	EA_a	η	ΔG
Z26	5.77	1.64	2.06	−0.54

Table S4 Predicted crystal data of investigated molecules.

Molecules	Space group	ρ	a(Å)	b(Å)	c(Å)	α	β	γ
H01	P1	1.02	15.38	8.84	19.85	91.50	81.35	75.11
H02	P1	1.02	19.25	31.84	4.78	85.54	82.83	71.44
H03	Pna21	1.08	31.27	8.92	19.97	90.00	90.00	90.00
H04	P212121	1.14	27.59	13.10	15.37	90.00	90.00	90.00

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