Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Effect of steric hindrance and number of substituents on transfer and interface properties of Y-shaped hole-transporting materials for perovskite solar cells

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Table S1 The HOMO and LUMO energies (eV) of Z34 obtained by different theoretical levels in THF solution.

Z34	HOMO (eV)	LUMO (eV)
Exp.[a]	**-5.14**	-2.43
B3LYP/6-31G**	**-4.45**	-1.46
M06/6-31G**	**-4.77**	-1.35
BMK/6-31G**	**-5.10**	-0.85
PBE0/6-31G**	**-4.68**	-1.41
O3LYP/6-31G**	4.15	**-1.65**
PW91/6-31G**	-3.88	**-2.15**
PW91/6-311G**	-4.12	**-2.40**

[a] from reference [12]

Table S2 Computed maximum absorption wavelengths (λ_{max} (nm), excited energy (eV) and oscillator strengths (*f*) of $S_0 \rightarrow S_1$ for the Z34 in THF.

Z34	λ_{max} (nm)	excited energy (eV)	oscillator strengths (*f*)
Exp.[a]	418	-	-
CAM-B3LYP/6-31G**	388.8	3.1889	2.7603
B3LYP/6-31G**	482.56	2.5693	2.1737
M06/6-31G**	459.04	2.7009	2.3459
BMK/6-31G**	413.08	3.0014	2.6393
PBE0/6-31G**	461.47	2.6867	2.333

[a] from reference [12]

Table S3 Computed maximum absorption wavelengths (λ_{max} (nm), excited energy (eV) and oscillator strengths (*f*) of $S_0 \rightarrow S_1$ for all molecules at BMK/6-31G** method in toluene.

molecules	λ_{max} (nm)	excited energy (eV)	oscillator strengths (*f*)
Z34	413.08	3.0014	2.6393
ZT1	400.36	3.0969	2.5443
ZT2	412.29	3.0072	2.6835
ZT3	400.09	3.0989	2.7605
ZT4	408.39	3.0359	2.6400

Table S4 The molecular orbital contribution to hole and electron distribution of Z34, ZT1, ZT2, ZT3 and ZT4.

Molecules	Excitation	Orbital contribution to hole		Orbital contribution to electron	
Z34	S_0-S_1	HOMO	73.300%	LUMO	75.302%
		HOMO-1	15.891%	LUMO+1	17.703
	S_0-S_2	HOMO	54.346%	LUMO	54.990%
		HOMO-1	35.087%	LUMO+1	34.335%
ZT1	S_0-S_1	HOMO	64.892%	LUMO	70.120%
		HOMO-1	20.804%	LUMO+1	21.396%
	S_0-S_2	HOMO	53.467%	LUMO	32.857%
		HOMO-1	32.659%	LUMO+1	55.246%
ZT2	S_0-S_1	HOMO	76.247%	LUMO	76.091%
		HOMO-1	14.406%	LUMO+1	16.219%
	S_0-S_2	HOMO	55.942%	LUMO	31.673%
		HOMO-1	32.260%	LUMO+1	56.914%
ZT3	S_0-S_1	HOMO	69.766%	LUMO	71.975%
		HOMO-1	18.517%	LUMO+1	19.450%
	S_0-S_2	HOMO	57.537%	LUMO	29.154%
		HOMO-1	29.297%	LUMO+1	57.830%
ZT4	S_0-S_1	HOMO	78.356%	LUMO	76.965%
		HOMO-1	13.302%	LUMO+1	14.857%
	S_0-S_2	HOMO	58.212%	LUMO	28.790
		HOMO-1	29.616%	LUMO+1	59.711

Table S5 Calculated Lattice parameters（Å）with the lowest total energies for the investigated molecules.

Molecules	Lattice parameters（Å）	
Z34	Cubic7.994×18.376×24.260 Å^3	α=114.686°, β=91.692°, γ=121.485°
ZT1	Cubic22.246×10.348×15.121 Å^3	α=106.694°, β=115.972°, γ=92.757°
ZT2	Cubic35.147×9.226×11.129Å3	α=90.000°, β=107.109°, γ=90.000°
ZT3	Cubic9.815×21.359×23.516 Å^3	α=90.000°, β=127.166°, γ=90.000°
ZT4	Cubic41.477×8.940×12.135 Å^3	α=90.000°, β=91.257°, γ=90.000°

Table S6 Contribution of each non-hydrogen atom to hole and electron of Z34.

S_0-S_1				S_0-S_2			
atom	hole	electron	Overlap	atom	hole	electron	Overlap
1(C)	1.61%	3.78%	2.47%	1(C)	1.08%	2.97%	1.79%
2(C)	2.40%	0.87%	1.45%	2(C)	1.18%	0.11%	0.36%
3(C)	3.30%	6.97%	4.79%	3(C)	1.85%	3.14%	2.41%
4(C)	2.81%	2.18%	2.47%	4(C)	1.24%	0.73%	0.95%
5(C)	1.62%	2.25%	1.91%	5(C)	1.28%	1.26%	1.27%
6(C)	4.60%	4.81%	4.71%	6(C)	2.24%	1.88%	2.05%
7(N)	10.91%	0.59%	2.53%	7(N)	5.47%	0.91%	2.24%
8(C)	2.87%	6.62%	4.36%	8(C)	2.32%	4.27%	3.15%
9(C)	2.35%	2.00%	2.17%	9(C)	1.23%	1.08%	1.15%
10(C)	1.48%	2.15%	1.79%	10(C)	1.55%	1.62%	1.58%
11(C)	4.07%	4.72%	4.38%	11(C)	2.62%	2.69%	2.66%
12(C)	1.22%	3.05%	1.93%	12(C)	1.37%	3.73%	2.26%
13(C)	2.39%	1.07%	1.60%	13(C)	1.21%	0.20%	0.50%
14(C)	0.68%	0.42%	0.53%	14(C)	0.68%	1.38%	0.97%
15(C)	1.34%	0.14%	0.44%	15(C)	0.78%	0.59%	0.68%
16(C)	0.13%	0.02%	0.05%	16(C)	0.20%	0.30%	0.24%
17(C)	1.25%	0.12%	0.39%	17(C)	0.93%	1.44%	1.16%
18(C)	0.18%	0.03%	0.07%	18(C)	0.20%	0.05%	0.10%
19(C)	1.57%	0.14%	0.48%	19(C)	1.02%	1.36%	1.18%
20(C)	3.30%	5.42%	4.23%	20(C)	4.65%	7.56%	5.93%

21(C)	3.93%	6.95%	5.22%	21(C)	3.51%	7.20%	5.03%
22(C)	2.55%	2.10%	2.31%	22(C)	4.44%	3.58%	3.99%
23(C)	1.24%	2.63%	1.81%	23(C)	1.52%	4.03%	2.47%
24(C)	0.99%	0.20%	0.44%	24(C)	1.95%	0.31%	0.77%
25(C)	2.01%	3.72%	2.74%	25(C)	2.94%	5.90%	4.17%
26(C)	1.08%	0.65%	0.84%	26(C)	2.17%	1.44%	1.77%
27(C)	1.34%	1.74%	1.53%	27(C)	1.61%	1.91%	1.75%
28(N)	3.19%	0.46%	1.21%	28(N)	6.56%	0.62%	2.01%
29(C)	0.20%	0.23%	0.21%	29(C)	0.51%	0.54%	0.53%
30(C)	0.36%	0.10%	0.19%	30(C)	0.81%	0.15%	0.34%
31(C)	0.05%	0.00%	0.01%	31(C)	0.10%	0.07%	0.09%
32(C)	0.32%	0.23%	0.27%	32(C)	0.76%	0.52%	0.63%
33(C)	0.06%	0.02%	0.00%	33(C)	0.17%	-0.04%	0.00%
34(C)	0.42%	0.21%	0.30%	34(C)	0.91%	0.49%	0.67%
35(O)	0.15%	0.04%	0.07%	35(O)	0.32%	0.08%	0.16%
36(C)	0.00%	0.00%	0.00%	36(C)	0.00%	0.00%	0.00%
38(C)	0.21%	0.26%	0.23%	38(C)	0.55%	0.61%	0.58%
39(C)	0.38%	0.19%	0.27%	39(C)	0.86%	0.41%	0.60%
40(C)	0.05%	0.01%	0.02%	40(C)	0.11%	0.07%	0.09%
41(C)	0.37%	0.23%	0.29%	41(C)	0.84%	0.52%	0.66%
42(C)	0.07%	0.02%	0.04%	42(C)	0.19%	0.08%	0.12%
43(C)	0.45%	0.20%	0.30%	43(C)	0.99%	0.41%	0.64%
44(O)	0.16%	0.04%	0.08%	44(O)	0.35%	0.08%	0.17%
45(C)	0.00%	0.00%	0.00%	45(C)	0.00%	0.00%	0.00%
47(C)	4.07%	6.73%	5.23%	47(C)	3.97%	6.60%	5.12%
48(C)	4.70%	7.99%	6.13%	48(C)	2.94%	5.71%	4.10%
49(C)	3.21%	2.73%	2.96%	49(C)	3.91%	3.44%	3.67%
50(C)	1.61%	1.99%	1.79%	50(C)	1.36%	1.44%	1.40%
51(C)	1.45%	0.94%	1.16%	51(C)	1.98%	1.57%	1.76%
52(C)	2.61%	4.77%	3.53%	52(C)	2.63%	5.58%	3.84%
53(C)	1.26%	0.25%	0.56%	53(C)	1.79%	0.26%	0.68%
54(C)	1.53%	3.37%	2.27%	54(C)	1.27%	3.82%	2.21%
55(N)	4.23%	0.54%	1.51%	55(N)	6.19%	0.52%	1.79%
56(C)	0.29%	0.29%	0.29%	56(C)	0.51%	0.46%	0.48%
57(C)	0.62%	0.35%	0.46%	57(C)	0.90%	0.51%	0.68%
58(C)	0.09%	0.02%	0.00%	58(C)	0.19%	0.00%	0.03%
59(C)	0.48%	0.28%	0.37%	59(C)	0.77%	0.41%	0.57%
60(C)	0.05%	0.06%	0.06%	60(C)	0.06%	0.13%	0.09%
61(C)	0.53%	0.11%	0.24%	61(C)	0.86%	0.15%	0.36%
62(C)	0.32%	0.38%	0.35%	62(C)	0.55%	0.61%	0.58%

63(C)	0.53%	0.21%	0.33%	63(C)	0.82%	0.19%	0.40%
64(C)	0.09%	0.05%	0.06%	64(C)	0.15%	0.11%	0.13%
65(C)	0.54%	0.34%	0.43%	65(C)	0.87%	0.49%	0.65%
66(C)	0.06%	0.02%	0.04%	66(C)	0.12%	-0.02%	0.00%
67(C)	0.72%	0.35%	0.50%	67(C)	1.08%	0.60%	0.80%
68(O)	0.21%	0.05%	0.11%	68(O)	0.35%	0.07%	0.16%
69(C)	0.00%	0.00%	0.00%	69(C)	0.00%	0.00%	0.00%
71(O)	0.18%	0.04%	0.09%	71(O)	0.31%	0.06%	0.14%
72(C)	0.00%	0.00%	0.00%	72(C)	0.00%	0.00%	0.00%
74(O)	0.40%	0.02%	0.09%	74(O)	0.45%	0.21%	0.31%
75(C)	0.00%	0.00%	0.00%	75(C)	0.00%	0.01%	0.00%

Table S7 Contribution of each non-hydrogen atom to hole and electron of ZT1.

S_0-S_1				S_0-S_2			
atom	hole	electron	Overlap	atom	hole	electron	Overlap
1(C)	1.48%	2.96%	2.09%	1(C)	1.18%	2.79%	1.81%
2(C)	1.55%	1.03%	1.26%	2(C)	1.14%	0.25%	0.53%
3(C)	2.95%	6.01%	4.21%	3(C)	2.15%	3.87%	2.88%
4(C)	1.77%	1.74%	1.76%	4(C)	1.20%	1.05%	1.12%
5(C)	1.50%	2.30%	1.86%	5(C)	1.33%	1.53%	1.42%
6(C)	3.12%	4.55%	3.77%	6(C)	2.17%	2.64%	2.39%
7(N)	8.17%	0.54%	2.10%	7(N)	6.33%	0.50%	1.79%
8(C)	3.02%	6.19%	4.32%	8(C)	2.29%	4.22%	3.11%
9(C)	1.71%	2.04%	1.87%	9(C)	1.30%	1.08%	1.19%
10(C)	1.65%	1.94%	1.79%	10(C)	1.33%	1.53%	1.42%
11(C)	3.27%	4.57%	3.87%	11(C)	2.35%	2.84%	2.58%
12(C)	1.40%	3.41%	2.19%	12(C)	1.27%	2.90%	1.92%
13(C)	1.79%	0.84%	1.22%	13(C)	1.24%	0.32%	0.63%
14(C)	0.30%	0.40%	0.34%	14(C)	0.52%	3.19%	1.28%
15(C)	1.57%	0.19%	0.55%	15(C)	1.46%	1.12%	1.28%
16(C)	0.02%	0.01%	0.02%	16(C)	0.08%	0.86%	0.26%
17(C)	1.40%	0.10%	0.38%	17(C)	1.62%	2.57%	2.04%
18(C)	0.03%	0.01%	0.02%	18(C)	0.08%	0.47%	0.20%
19(C)	1.49%	0.17%	0.51%	19(C)	1.38%	1.40%	1.39%
20(C)	4.27%	6.07%	5.09%	20(C)	4.20%	6.17%	5.09%

21(C)	3.81%	7.44%	5.32%	21(C)	2.98%	6.38%	4.36%
22(C)	3.51%	2.49%	2.96%	22(C)	4.10%	2.92%	3.46%
23(C)	1.37%	3.03%	2.04%	23(C)	1.27%	3.25%	2.03%
24(C)	1.47%	0.26%	0.62%	24(C)	1.83%	0.29%	0.73%
25(C)	2.50%	4.45%	3.34%	25(C)	2.60%	5.07%	3.63%
26(C)	1.60%	0.81%	1.14%	26(C)	2.04%	1.10%	1.50%
27(C)	1.48%	1.95%	1.70%	27(C)	1.37%	1.81%	1.57%
28(N)	4.69%	0.53%	1.58%	28(N)	6.00%	0.54%	1.80%
29(C)	0.39%	0.37%	0.38%	29(C)	0.55%	0.47%	0.50%
30(C)	0.61%	0.20%	0.35%	30(C)	0.84%	0.23%	0.44%
31(C)	0.10%	0.06%	0.08%	31(C)	0.09%	0.13%	0.11%
32(C)	0.62%	0.37%	0.48%	32(C)	0.83%	0.45%	0.61%
33(C)	0.13%	0.03%	0.06%	33(C)	0.19%	0.03%	0.07%
34(C)	0.72%	0.35%	0.50%	34(C)	0.93%	0.49%	0.68%
35(O)	0.26%	0.06%	0.12%	35(O)	0.31%	0.07%	0.14%
36(C)	0.00%	0.00%	0.00%	36(C)	0.00%	0.00%	0.00%
38(C)	0.37%	0.35%	0.36%	38(C)	0.48%	0.45%	0.46%
39(C)	0.56%	0.20%	0.34%	39(C)	0.76%	0.29%	0.47%
40(C)	0.10%	0.04%	0.07%	40(C)	0.09%	0.04%	0.06%
41(C)	0.60%	0.33%	0.44%	41(C)	0.78%	0.40%	0.56%
42(C)	0.13%	0.02%	0.05%	42(C)	0.20%	0.04%	0.09%
43(C)	0.67%	0.29%	0.44%	43(C)	0.82%	0.33%	0.52%
44(O)	0.24%	0.05%	0.11%	44(O)	0.29%	0.06%	0.14%
45(C)	0.00%	0.00%	0.00%	45(C)	0.00%	0.00%	0.00%
47(C)	4.16%	6.17%	5.06%	47(C)	4.13%	6.34%	5.11%
48(C)	3.65%	7.37%	5.18%	48(C)	2.79%	6.23%	4.17%
49(C)	3.48%	2.69%	3.06%	49(C)	4.13%	3.25%	3.66%
50(C)	1.42%	1.87%	1.63%	50(C)	1.30%	1.69%	1.48%
51(C)	1.57%	0.96%	1.23%	51(C)	2.04%	1.36%	1.66%
52(C)	2.48%	4.71%	3.42%	52(C)	2.62%	5.53%	3.81%
53(C)	1.50%	0.28%	0.65%	53(C)	1.94%	0.35%	0.82%
54(C)	1.33%	3.24%	2.08%	54(C)	1.24%	3.56%	2.10%
55(N)	4.93%	0.51%	1.59%	55(N)	6.51%	0.53%	1.86%
56(C)	0.42%	0.33%	0.37%	56(C)	0.58%	0.43%	0.50%
57(C)	0.78%	0.35%	0.52%	57(C)	1.01%	0.49%	0.70%
58(C)	0.15%	0.04%	0.07%	58(C)	0.23%	0.03%	0.08%
59(C)	0.68%	0.33%	0.47%	59(C)	0.92%	0.39%	0.60%
60(C)	0.11%	0.07%	0.09%	60(C)	0.10%	0.13%	0.11%
61(C)	0.65%	0.20%	0.36%	61(C)	0.92%	0.21%	0.44%
62(C)	0.44%	0.39%	0.41%	62(C)	0.58%	0.54%	0.56%

63(C)	0.62%	0.19%	0.34%	63(C)	0.81%	0.20%	0.40%
64(C)	0.12%	0.03%	0.06%	64(C)	0.17%	0.06%	0.10%
65(C)	0.65%	0.35%	0.47%	65(C)	0.88%	0.46%	0.64%
66(C)	0.09%	-0.01%	0.00%	66(C)	0.12%	-0.01%	0.00%
67(C)	0.85%	0.31%	0.52%	67(C)	1.12%	0.47%	0.72%
68(O)	0.30%	0.06%	0.13%	68(O)	0.37%	0.07%	0.16%
69(C)	0.00%	0.00%	0.00%	69(C)	0.00%	0.00%	0.00%
71(O)	0.28%	0.05%	0.12%	71(O)	0.37%	0.06%	0.15%
72(C)	0.00%	0.00%	0.00%	72(C)	0.00%	0.00%	0.00%
122(S)	0.13%	0.03%	0.06%	122(S)	0.23%	0.38%	0.29%
123(O)	0.10%	0.01%	0.02%	123(O)	0.09%	0.04%	0.06%
124(C)	0.10%	0.01%	0.04%	124(C)	0.16%	0.30%	0.22%
125(C)	0.02%	0.00%	0.00%	125(C)	0.03%	0.05%	0.04%
126(C)	0.01%	0.00%	0.00%	126(C)	0.01%	0.02%	0.01%
127(C)	0.00%	0.00%	0.00%	127(C)	0.01%	0.01%	0.01%
128(C)	0.00%	0.00%	0.00%	128(C)	0.00%	0.00%	0.00%
129(C)	0.00%	0.00%	0.00%	129(C)	0.00%	0.00%	0.00%

Table S8 Contribution of each non-hydrogen atom to hole and electron of ZT2.

S_0-S_1				S_0-S_2			
atom	hole	electron	Overlap	atom	hole	electron	Overlap
1(C)	1.42%	3.60%	2.26%	1(C)	1.19%	2.91%	1.86%
2(C)	2.74%	0.87%	1.54%	2(C)	1.37%	0.13%	0.43%
3(C)	3.26%	6.92%	4.75%	3(C)	2.19%	3.42%	2.74%
4(C)	3.07%	2.12%	2.55%	4(C)	1.53%	0.70%	1.04%
5(C)	1.51%	2.17%	1.81%	5(C)	1.35%	1.45%	1.40%
6(C)	5.05%	4.61%	4.83%	6(C)	2.87%	1.88%	2.32%
7(N)	12.20%	0.56%	2.62%	7(N)	6.20%	0.98%	2.46%
8(C)	3.12%	6.86%	4.63%	8(C)	2.26%	3.57%	2.84%
9(C)	2.77%	2.02%	2.37%	9(C)	1.44%	0.76%	1.05%
10(C)	1.56%	2.32%	1.90%	10(C)	1.46%	1.53%	1.50%
11(C)	4.77%	4.64%	4.70%	11(C)	2.90%	2.05%	2.44%
12(C)	1.28%	3.13%	2.00%	12(C)	1.29%	3.17%	2.02%
13(C)	2.71%	1.07%	1.70%	13(C)	1.34%	0.15%	0.45%
14(C)	0.92%	0.37%	0.58%	14(C)	0.75%	1.28%	0.98%
15(C)	1.81%	0.14%	0.51%	15(C)	1.12%	0.99%	1.05%
16(C)	0.26%	0.02%	0.06%	16(C)	0.22%	0.14%	0.18%
17(C)	1.46%	0.07%	0.31%	17(C)	0.99%	1.43%	1.19%

18(C)	0.20%	0.02%	0.07%	18(C)	0.20%	0.13%	0.17%
19(C)	1.48%	0.12%	0.42%	19(C)	0.85%	0.91%	0.88%
20(C)	3.15%	5.88%	4.30%	20(C)	4.02%	7.24%	5.39%
21(C)	4.58%	6.85%	5.61%	21(C)	3.69%	5.89%	4.66%
22(C)	2.13%	2.66%	2.38%	22(C)	3.50%	4.26%	3.86%
23(C)	1.31%	2.60%	1.84%	23(C)	1.39%	3.37%	2.16%
24(C)	0.79%	0.34%	0.52%	24(C)	1.55%	0.63%	0.98%
25(C)	2.27%	4.13%	3.06%	25(C)	2.98%	6.14%	4.28%
26(C)	0.83%	0.90%	0.87%	26(C)	1.63%	1.75%	1.69%
27(C)	1.51%	1.94%	1.71%	27(C)	1.63%	2.08%	1.84%
28(N)	2.88%	0.29%	0.91%	28(N)	6.18%	0.34%	1.46%
29(C)	0.14%	0.54%	0.27%	29(C)	0.37%	1.29%	0.69%
30(C)	0.63%	0.32%	0.45%	30(C)	1.36%	0.68%	0.96%
31(C)	0.01%	0.09%	0.03%	31(C)	0.04%	0.23%	0.10%
32(C)	0.55%	0.45%	0.50%	32(C)	1.35%	1.10%	1.22%
33(C)	0.02%	0.11%	0.04%	33(C)	0.06%	0.33%	0.14%
34(C)	0.53%	0.24%	0.36%	34(C)	1.22%	0.45%	0.74%
35(S)	0.05%	0.06%	0.06%	35(S)	0.17%	0.15%	0.16%
36(C)	0.22%	0.24%	0.23%	36(C)	0.52%	0.36%	0.43%
37(C)	0.37%	0.09%	0.18%	37(C)	0.78%	0.14%	0.32%
38(C)	0.03%	0.04%	0.03%	38(C)	0.08%	0.03%	0.05%
39(C)	0.32%	0.18%	0.24%	39(C)	0.74%	0.19%	0.37%
40(C)	0.07%	0.00%	0.01%	40(C)	0.18%	0.02%	0.05%
41(C)	0.38%	0.19%	0.27%	41(C)	0.85%	0.23%	0.44%
42(O)	0.11%	0.03%	0.05%	42(O)	0.29%	0.03%	0.09%
43(C)	3.27%	6.32%	4.55%	43(C)	3.82%	6.78%	5.09%
44(C)	4.82%	7.25%	5.91%	44(C)	3.57%	5.50%	4.43%
45(C)	2.26%	2.74%	2.49%	45(C)	3.32%	3.95%	3.62%
46(C)	1.53%	2.05%	1.77%	46(C)	1.50%	1.94%	1.71%
47(C)	0.93%	0.83%	0.88%	47(C)	1.58%	1.52%	1.55%
48(C)	2.35%	4.29%	3.18%	48(C)	2.83%	5.71%	4.02%
49(C)	0.86%	0.40%	0.58%	49(C)	1.47%	0.60%	0.94%
50(C)	1.40%	2.76%	1.97%	50(C)	1.36%	3.18%	2.08%
51(N)	3.15%	0.32%	1.01%	51(N)	5.65%	0.34%	1.38%
52(C)	0.15%	0.55%	0.29%	52(C)	0.32%	1.26%	0.63%
53(C)	0.62%	0.31%	0.44%	53(C)	1.13%	0.55%	0.78%
54(C)	0.02%	0.12%	0.05%	54(C)	0.05%	0.29%	0.12%
55(C)	0.63%	0.46%	0.54%	55(C)	1.22%	1.05%	1.13%
56(C)	0.02%	0.09%	0.04%	56(C)	0.03%	0.27%	0.09%
57(C)	0.66%	0.30%	0.44%	57(C)	1.22%	0.54%	0.82%

58(C)	0.24%	0.21%	0.23%	58(C)	0.52%	0.32%	0.41%
59(C)	0.32%	0.14%	0.21%	59(C)	0.61%	0.09%	0.23%
60(C)	0.07%	0.01%	0.02%	60(C)	0.13%	0.00%	0.00%
61(C)	0.34%	0.15%	0.23%	61(C)	0.65%	0.17%	0.33%
62(C)	0.05%	0.02%	0.04%	62(C)	0.10%	-0.02%	0.00%
63(C)	0.43%	0.11%	0.22%	63(C)	0.83%	0.15%	0.36%
64(O)	0.12%	0.03%	0.06%	64(O)	0.24%	0.03%	0.08%
65(S)	0.07%	0.06%	0.06%	65(S)	0.17%	0.14%	0.15%
106(C)	0.05%	0.04%	0.04%	106(C)	0.11%	0.10%	0.10%
107(C)	0.00%	0.00%	0.00%	107(C)	0.01%	0.00%	0.01%
108(C)	0.00%	0.00%	0.00%	108(C)	0.00%	0.00%	0.00%
109(C)	0.00%	0.00%	0.00%	109(C)	0.00%	0.00%	0.00%
110(C)	0.00%	0.00%	0.00%	110(C)	0.00%	0.00%	0.00%
111(C)	0.00%	0.00%	0.00%	111(C)	0.00%	0.00%	0.00%
113(O)	0.01%	0.01%	0.01%	113(O)	0.12%	0.02%	0.05%
114(C)	0.04%	0.04%	0.04%	114(C)	0.11%	0.11%	0.11%
115(C)	0.01%	0.01%	0.01%	115(C)	0.03%	0.02%	0.02%
116(C)	0.00%	0.00%	0.00%	116(C)	0.01%	0.01%	0.01%
117(C)	0.00%	0.00%	0.00%	117(C)	0.00%	0.00%	0.00%
118(C)	0.00%	0.00%	0.00%	118(C)	0.00%	0.00%	0.00%
119(C)	0.00%	0.00%	0.00%	119(C)	0.00%	0.00%	0.00%
121(O)	-0.01%	0.01%	0.00%	121(O)	0.09%	0.02%	0.04%
146(C)	0.00%	0.00%	0.00%	146(C)	0.00%	0.00%	0.00%
147(O)	0.57%	0.01%	0.09%	147(O)	0.48%	0.22%	0.33%
148(C)	0.00%	0.00%	0.00%	148(C)	0.00%	0.00%	0.00%
152(C)	0.00%	0.00%	0.00%	152(C)	0.00%	0.00%	0.00%

Table S9 Contribution of each non-hydrogen atom to hole and electron of ZT3.

S_0-S_1				S_0-S_2			
atom	hole	electron	Overlap	atom	hole	electron	Overlap
1(C)	1.61%	3.38%	2.33%	1(C)	1.15%	2.63%	1.74%
2(C)	1.98%	0.93%	1.36%	2(C)	1.42%	0.18%	0.50%
3(C)	3.36%	6.61%	4.71%	3(C)	2.25%	3.61%	2.85%
4(C)	2.25%	1.99%	2.12%	4(C)	1.56%	1.00%	1.25%
5(C)	1.68%	2.34%	1.98%	5(C)	1.31%	1.32%	1.31%
6(C)	4.14%	4.70%	4.41%	6(C)	2.72%	2.19%	2.44%
7(N)	9.63%	0.55%	2.30%	7(N)	7.58%	0.57%	2.08%
8(C)	3.12%	6.06%	4.35%	8(C)	2.62%	4.29%	3.35%

9(C)	2.09%	1.85%	1.96%	9(C)	1.62%	1.10%	1.33%
10(C)	1.56%	2.03%	1.78%	10(C)	1.46%	1.49%	1.48%
11(C)	3.79%	4.34%	4.06%	11(C)	3.01%	2.69%	2.84%
12(C)	1.35%	3.01%	2.02%	12(C)	1.37%	3.05%	2.05%
13(C)	2.09%	0.92%	1.39%	13(C)	1.52%	0.29%	0.67%
14(C)	0.36%	0.38%	0.37%	14(C)	0.61%	3.44%	1.45%
15(C)	1.69%	0.15%	0.50%	15(C)	1.60%	1.31%	1.45%
16(C)	0.03%	0.02%	0.03%	16(C)	0.09%	0.97%	0.29%
17(C)	1.53%	0.10%	0.39%	17(C)	1.73%	2.94%	2.26%
18(C)	0.03%	-0.01%	0.00%	18(C)	0.10%	0.56%	0.23%
19(C)	1.65%	0.15%	0.50%	19(C)	1.52%	1.57%	1.54%
20(C)	3.69%	5.67%	4.57%	20(C)	4.15%	6.38%	5.15%
21(C)	4.12%	6.64%	5.23%	21(C)	3.64%	6.01%	4.68%
22(C)	2.69%	2.61%	2.65%	22(C)	3.63%	3.49%	3.56%
23(C)	1.30%	2.57%	1.83%	23(C)	1.38%	2.96%	2.02%
24(C)	1.07%	0.34%	0.60%	24(C)	1.59%	0.53%	0.92%
25(C)	2.48%	4.19%	3.23%	25(C)	2.92%	5.37%	3.96%
26(C)	1.16%	0.88%	1.01%	26(C)	1.71%	1.33%	1.51%
27(C)	1.47%	1.90%	1.67%	27(C)	1.56%	2.01%	1.77%
28(N)	3.66%	0.31%	1.07%	28(N)	5.85%	0.34%	1.40%
29(C)	0.17%	0.64%	0.33%	29(C)	0.33%	1.24%	0.64%
30(C)	0.75%	0.27%	0.45%	30(C)	1.24%	0.57%	0.84%
31(C)	0.02%	0.15%	0.06%	31(C)	0.03%	0.25%	0.09%
32(C)	0.69%	0.56%	0.63%	32(C)	1.21%	1.04%	1.12%
33(C)	0.03%	0.05%	0.04%	33(C)	0.05%	0.26%	0.12%
34(C)	0.66%	0.31%	0.45%	34(C)	1.10%	0.47%	0.72%
35(S)	0.12%	0.09%	0.10%	35(S)	0.16%	0.16%	0.16%
36(C)	0.27%	0.20%	0.24%	36(C)	0.48%	0.26%	0.35%
37(C)	0.45%	0.06%	0.16%	37(C)	0.70%	0.08%	0.24%
38(C)	0.03%	0.01%	0.01%	38(C)	0.07%	0.04%	0.05%
39(C)	0.37%	0.13%	0.21%	39(C)	0.64%	0.15%	0.31%
40(C)	0.08%	-0.02%	0.00%	40(C)	0.15%	-0.01%	0.00%
41(C)	0.47%	0.15%	0.26%	41(C)	0.77%	0.18%	0.38%
42(O)	0.12%	0.02%	0.05%	42(O)	0.22%	0.02%	0.07%
43(C)	0.00%	0.00%	0.00%	43(C)	0.00%	0.00%	0.00%
45(C)	4.00%	6.59%	5.13%	45(C)	3.55%	5.79%	4.53%
46(C)	4.51%	7.46%	5.80%	46(C)	3.14%	5.16%	4.03%
47(C)	2.97%	3.12%	3.05%	47(C)	3.20%	3.40%	3.30%
48(C)	1.65%	2.12%	1.87%	48(C)	1.38%	1.73%	1.54%
49(C)	1.21%	1.14%	1.17%	49(C)	1.44%	1.41%	1.42%

50(C)	2.73%	4.97%	3.68%	50(C)	2.57%	5.13%	3.63%
51(C)	1.12%	0.40%	0.67%	51(C)	1.35%	0.46%	0.79%
52(C)	1.49%	3.12%	2.16%	52(C)	1.23%	2.89%	1.89%
53(N)	4.16%	0.34%	1.19%	53(N)	5.32%	0.31%	1.28%
54(C)	0.20%	0.62%	0.35%	54(C)	0.26%	0.94%	0.50%
55(C)	0.85%	0.31%	0.51%	55(C)	1.05%	0.39%	0.64%
56(C)	0.03%	0.12%	0.06%	56(C)	0.04%	0.20%	0.09%
57(C)	0.86%	0.54%	0.68%	57(C)	1.10%	0.81%	0.94%
58(C)	0.02%	0.09%	0.04%	58(C)	0.02%	0.17%	0.05%
59(C)	0.89%	0.32%	0.53%	59(C)	1.14%	0.41%	0.69%
60(C)	0.36%	0.25%	0.30%	60(C)	0.44%	0.26%	0.34%
61(C)	0.45%	0.12%	0.23%	61(C)	0.56%	0.13%	0.27%
62(C)	0.09%	0.01%	0.02%	62(C)	0.12%	-0.04%	0.00%
63(C)	0.46%	0.17%	0.28%	63(C)	0.59%	0.15%	0.29%
64(C)	0.06%	0.01%	0.02%	64(C)	0.08%	0.00%	0.00%
65(C)	0.63%	0.13%	0.29%	65(C)	0.77%	0.09%	0.26%
66(O)	0.19%	0.03%	0.07%	66(O)	0.22%	0.03%	0.08%
67(C)	0.00%	0.00%	0.00%	67(C)	0.00%	0.00%	0.00%
69(S)	0.09%	0.07%	0.08%	69(S)	0.11%	0.12%	0.12%
114(S)	0.14%	0.03%	0.06%	114(S)	0.24%	0.43%	0.32%
115(O)	0.10%	0.00%	0.02%	115(O)	0.10%	0.04%	0.07%
116(C)	0.12%	0.01%	0.04%	116(C)	0.17%	0.32%	0.23%
117(C)	0.03%	0.00%	0.01%	117(C)	0.04%	0.06%	0.05%
118(C)	0.01%	0.00%	0.00%	118(C)	0.01%	0.02%	0.02%
119(C)	0.00%	0.00%	0.00%	119(C)	0.01%	0.01%	0.01%
120(C)	0.00%	0.00%	0.00%	120(C)	0.00%	0.00%	0.00%
121(C)	0.00%	0.00%	0.00%	121(C)	0.00%	0.00%	0.00%
135(C)	0.07%	0.05%	0.06%	135(C)	0.08%	0.08%	0.08%
136(C)	0.01%	0.00%	0.00%	136(C)	0.01%	0.00%	0.01%
137(C)	0.00%	0.00%	0.00%	137(C)	0.00%	0.00%	0.00%
138(C)	0.00%	0.00%	0.00%	138(C)	0.00%	0.00%	0.00%
139(C)	0.00%	0.00%	0.00%	139(C)	0.00%	0.00%	0.00%
140(C)	0.00%	0.00%	0.00%	140(C)	0.00%	0.00%	0.00%
142(O)	-0.01%	0.01%	0.00%	142(O)	0.05%	0.02%	0.03%
143(C)	0.07%	0.06%	0.06%	143(C)	0.10%	0.11%	0.11%
144(C)	0.01%	0.01%	0.01%	144(C)	0.02%	0.02%	0.02%
145(C)	0.00%	0.00%	0.00%	145(C)	0.01%	0.01%	0.01%
146(C)	0.00%	0.00%	0.00%	146(C)	0.00%	0.00%	0.00%
147(C)	0.00%	0.00%	0.00%	147(C)	0.00%	0.00%	0.00%
148(C)	0.00%	0.00%	0.00%	148(C)	0.00%	0.00%	0.00%

150(O)	0.11%	0.01%	0.04%	150(O)	0.10%	0.02%	0.05%

Table S10 Contribution of each non-hydrogen atom to hole and electron of ZT4.

S_0-S_1				S_0-S_2			
atom	hole	electron	Overlap	atom	hole	electron	Overlap
1(C)	1.52%	3.92%	2.44%	1(C)	1.19%	2.60%	1.76%
2(C)	3.17%	0.89%	1.68%	2(C)	1.61%	0.14%	0.48%
3(C)	3.63%	7.41%	5.19%	3(C)	2.21%	2.98%	2.57%
4(C)	3.47%	2.15%	2.73%	4(C)	1.79%	0.53%	0.97%
5(C)	1.65%	2.28%	1.94%	5(C)	1.36%	1.30%	1.33%
6(C)	5.86%	4.72%	5.26%	6(C)	3.29%	1.45%	2.19%
7(N)	13.37%	0.56%	2.73%	7(N)	7.31%	1.06%	2.79%
8(C)	3.05%	6.71%	4.53%	8(C)	2.70%	3.96%	3.27%
9(C)	2.93%	1.94%	2.39%	9(C)	1.75%	0.84%	1.21%
10(C)	1.42%	2.29%	1.80%	10(C)	1.60%	1.68%	1.64%
11(C)	4.95%	4.53%	4.74%	11(C)	3.62%	2.21%	2.83%
12(C)	1.15%	2.82%	1.80%	12(C)	1.41%	3.39%	2.19%
13(C)	2.99%	1.13%	1.84%	13(C)	1.69%	0.17%	0.54%
14(C)	1.00%	0.33%	0.57%	14(C)	0.92%	1.37%	1.13%
15(C)	1.92%	0.11%	0.47%	15(C)	1.25%	1.03%	1.14%
16(C)	0.23%	0.00%	0.03%	16(C)	0.29%	0.12%	0.19%
17(C)	1.46%	0.02%	0.16%	17(C)	1.14%	1.52%	1.32%
18(C)	0.23%	0.01%	0.05%	18(C)	0.26%	0.10%	0.16%
19(C)	1.49%	0.09%	0.37%	19(C)	0.95%	0.93%	0.94%
20(C)	2.61%	5.38%	3.75%	20(C)	4.06%	7.69%	5.59%
21(C)	4.46%	6.28%	5.29%	21(C)	4.49%	6.25%	5.29%
22(C)	1.64%	2.52%	2.03%	22(C)	3.21%	4.58%	3.83%
23(C)	1.20%	2.35%	1.68%	23(C)	1.57%	3.54%	2.36%
24(C)	0.59%	0.39%	0.48%	24(C)	1.35%	0.76%	1.01%
25(C)	1.98%	3.61%	2.68%	25(C)	3.17%	6.24%	4.45%
26(C)	0.62%	0.79%	0.70%	26(C)	1.44%	1.91%	1.66%
27(C)	1.32%	1.69%	1.49%	27(C)	1.74%	1.97%	1.85%
28(N)	2.14%	0.23%	0.70%	28(N)	5.43%	0.33%	1.34%
29(C)	0.11%	0.35%	0.19%	29(C)	0.34%	0.90%	0.55%
30(C)	0.40%	0.12%	0.22%	30(C)	1.02%	0.34%	0.59%
31(C)	0.01%	0.11%	0.03%	31(C)	0.03%	0.18%	0.08%
32(C)	0.34%	0.29%	0.32%	32(C)	0.96%	0.68%	0.81%
33(C)	0.02%	-0.02%	0.00%	33(C)	0.05%	0.11%	0.08%

34(C)	0.33%	0.18%	0.24%	34(C)	0.90%	0.36%	0.57%
35(S)	0.04%	0.03%	0.04%	35(S)	0.11%	0.11%	0.11%
36(C)	0.10%	0.35%	0.19%	36(C)	0.33%	0.90%	0.54%
37(C)	0.41%	0.18%	0.27%	37(C)	1.04%	0.48%	0.70%
38(C)	0.01%	0.06%	0.02%	38(C)	0.03%	0.06%	0.04%
39(C)	0.35%	0.27%	0.31%	39(C)	0.99%	0.64%	0.80%
40(C)	0.02%	0.05%	0.03%	40(C)	0.05%	0.22%	0.11%
41(C)	0.34%	0.14%	0.22%	41(C)	0.93%	0.20%	0.43%
42(S)	0.04%	0.02%	0.03%	42(S)	0.09%	0.08%	0.09%
43(C)	3.29%	6.99%	4.80%	43(C)	3.44%	6.62%	4.77%
44(C)	5.51%	7.56%	6.45%	44(C)	3.86%	4.91%	4.35%
45(C)	2.05%	3.19%	2.56%	45(C)	2.69%	4.01%	3.29%
46(C)	1.70%	2.04%	1.87%	46(C)	1.50%	1.52%	1.51%
47(C)	0.75%	1.07%	0.90%	47(C)	1.20%	1.84%	1.48%
48(C)	2.53%	4.54%	3.39%	48(C)	2.76%	5.36%	3.84%
49(C)	0.69%	0.45%	0.56%	49(C)	1.09%	0.55%	0.78%
50(C)	1.57%	3.10%	2.20%	50(C)	1.41%	3.27%	2.15%
51(N)	2.67%	0.27%	0.85%	51(N)	4.64%	0.27%	1.12%
52(C)	0.13%	0.40%	0.23%	52(C)	0.26%	0.69%	0.42%
53(C)	0.42%	0.24%	0.32%	53(C)	0.75%	0.39%	0.54%
54(C)	0.02%	0.05%	0.03%	54(C)	0.04%	0.08%	0.05%
55(C)	0.44%	0.33%	0.38%	55(C)	0.79%	0.55%	0.66%
56(C)	0.01%	0.10%	0.03%	56(C)	0.02%	0.19%	0.07%
57(C)	0.48%	0.18%	0.29%	57(C)	0.82%	0.23%	0.43%
58(C)	0.15%	0.44%	0.26%	58(C)	0.30%	0.78%	0.48%
59(C)	0.46%	0.14%	0.26%	59(C)	0.83%	0.17%	0.38%
60(C)	0.03%	0.12%	0.06%	60(C)	0.05%	0.24%	0.11%
61(C)	0.51%	0.33%	0.41%	61(C)	0.92%	0.50%	0.68%
62(C)	0.02%	0.03%	0.02%	62(C)	0.03%	0.04%	0.03%
63(C)	0.54%	0.28%	0.39%	63(C)	0.94%	0.49%	0.68%
64(S)	0.08%	0.04%	0.06%	64(S)	0.13%	0.07%	0.10%
65(S)	0.04%	0.03%	0.04%	65(S)	0.08%	0.08%	0.08%
106(C)	0.03%	0.02%	0.03%	106(C)	0.06%	0.05%	0.05%
107(C)	0.00%	0.00%	0.00%	107(C)	0.01%	0.00%	0.00%
108(C)	0.00%	0.00%	0.00%	108(C)	0.00%	0.00%	0.00%
109(C)	0.00%	0.00%	0.00%	109(C)	0.00%	0.00%	0.00%
110(C)	0.00%	0.00%	0.00%	110(C)	0.00%	0.00%	0.00%
111(C)	0.00%	0.00%	0.00%	111(C)	0.00%	0.00%	0.00%
113(O)	0.00%	0.01%	0.00%	113(O)	0.01%	0.01%	0.01%
114(C)	0.03%	0.03%	0.03%	114(C)	0.08%	0.07%	0.07%

115(C)	0.01%	0.00%	0.00%	115(C)	0.02%	0.01%	0.01%
116(C)	0.00%	0.00%	0.00%	116(C)	0.00%	0.00%	0.00%
117(C)	0.00%	0.00%	0.00%	117(C)	0.00%	0.00%	0.00%
118(C)	0.00%	0.00%	0.00%	118(C)	0.00%	0.00%	0.00%
119(C)	0.00%	0.00%	0.00%	119(C)	0.00%	0.00%	0.00%
121(O)	0.02%	0.00%	0.01%	121(O)	0.05%	0.02%	0.03%
146(C)	0.03%	0.03%	0.03%	146(C)	0.08%	0.07%	0.08%
147(C)	0.01%	0.00%	0.01%	147(C)	0.02%	0.01%	0.02%
148(C)	0.00%	0.00%	0.00%	148(C)	0.01%	0.00%	0.01%
149(C)	0.00%	0.00%	0.00%	149(C)	0.00%	0.00%	0.00%
150(C)	0.00%	0.00%	0.00%	150(C)	0.00%	0.00%	0.00%
151(C)	0.00%	0.00%	0.00%	151(C)	0.00%	0.00%	0.00%
153(O)	0.01%	0.00%	0.00%	153(O)	0.03%	0.00%	0.01%
154(C)	0.05%	0.03%	0.04%	154(C)	0.08%	0.05%	0.06%
155(C)	0.01%	0.00%	0.01%	155(C)	0.02%	0.01%	0.01%
156(C)	0.00%	0.00%	0.00%	156(C)	0.01%	0.00%	0.00%
157(C)	0.00%	0.00%	0.00%	157(C)	0.00%	0.00%	0.00%
158(C)	0.00%	0.00%	0.00%	158(C)	0.00%	0.00%	0.00%
159(C)	0.00%	0.00%	0.00%	159(C)	0.00%	0.00%	0.00%
161(O)	0.05%	0.01%	0.02%	161(O)	0.09%	0.01%	0.03%
186(O)	0.58%	0.01%	0.06%	186(O)	0.60%	0.24%	0.38%
187(C)	0.00%	0.00%	0.00%	187(C)	0.00%	0.00%	0.00%

Table S11 The electronic coupling (V, eV)/transfer integral (v, eV) and hole mobility (μ, $cm^2\ V^{-1}\ s^{-1}$) at different method

Compounds	Pathways	electronic coupling (V, eV)	μ_1	transfer integral (v, eV)	μ_2
Z34	T_1	3.62×10^{-6}	1.36×10^{-4}	5.44×10^{-3}	0.115
	T_2	0		9.52×10^{-3}	
	T_3	3.17×10^{-4}		2.99×10^{-2}	
	T_4	0		3.13×10^{-3}	

Table S12 The electronic coupling (V, eV) and hole mobility (μ, $cm^2\ V^{-1}\ s^{-1}$) of the Z34 molecules on PW91/6-31G** and PBE0/6-31G** method.

Compounds	Pathways	V (eV)	Φ	μ ($cm^2V^{-1}s^{-1}$)
PBE0	T_1	3.62×10^{-6}	115°	7.6×10^{-4} (*Expt.*)
	T_2	0		
	T_3	3.17×10^{-4}		1.36×10^{-4}
	T_4	0		
PW91	T_1	3.47×10^{-6}	115°	1.35×10^{-4}
	T_2	0		
	T_3	3.16×10^{-4}		
	T_4	0		

Table S13 The optimized configurations of ZT-based HTMs adsorbed on the PbI_2-terminated perovskite surface, together with the corresponding adsorption energy (Kcal/mol) and O···Pb distances(Å) of Z34, ZT1, ZT2, ZT3 and ZT4.

Molecules	adsorption energy (Kcal/mol)	O···Pb distances 1 (Å)	O···Pb distances 2 (Å)
Z34	-53.482	4.200	3.909
ZT1	-51.322	5.417	4.748
ZT2	-57.506	3.949	4.501
ZT3	-63.753	4.589	4.678
ZT4	-50.610	3.965	4.329

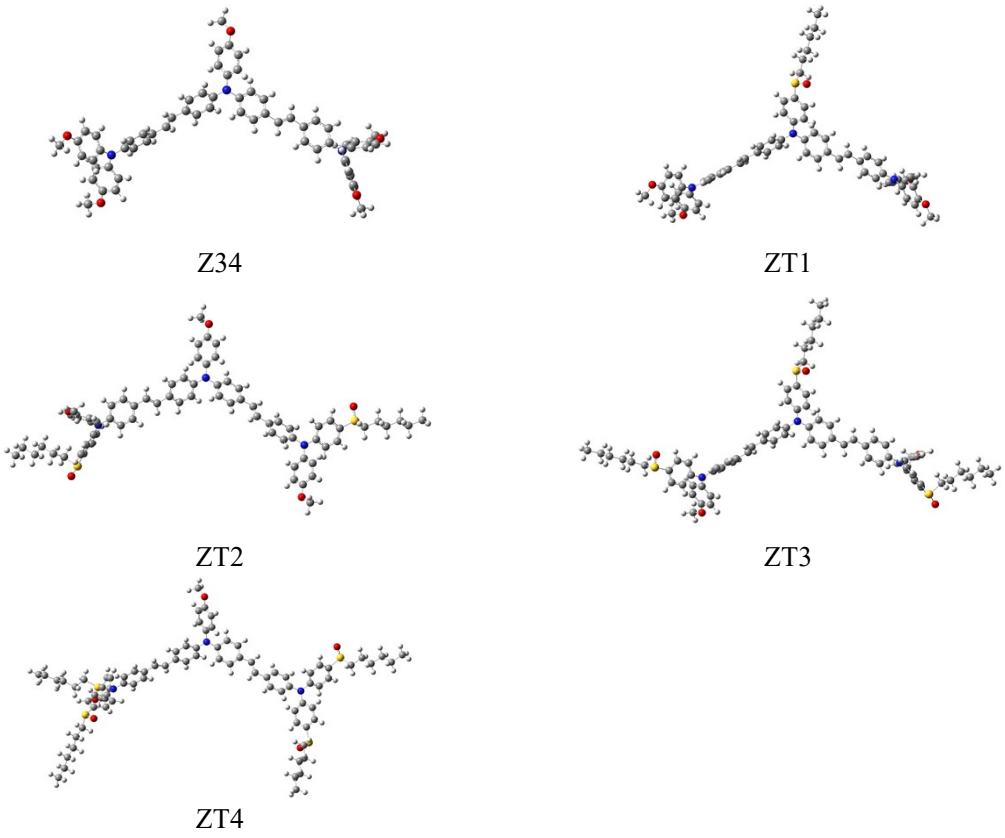

Fig. S1 The optimized geometries of the investigated molecules at the BMK/6-31G** level.

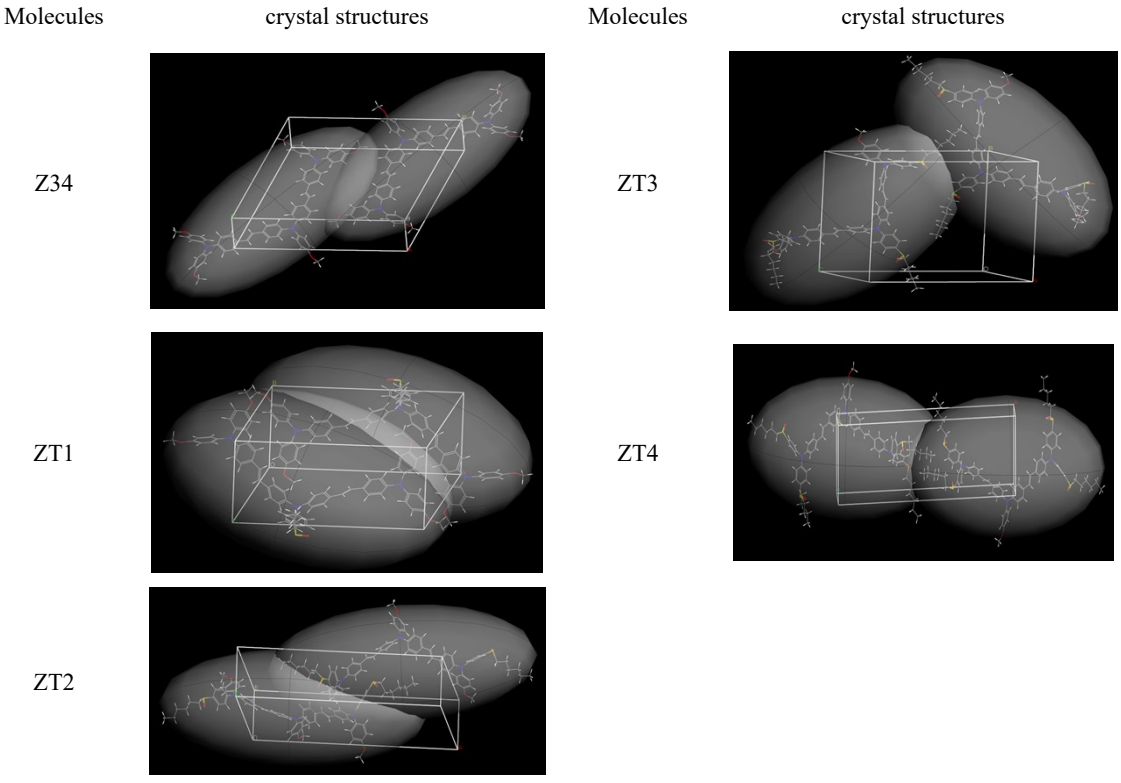

Fig. S2 Calculated crystal structures with the lowest total energies of the investigated molecules.

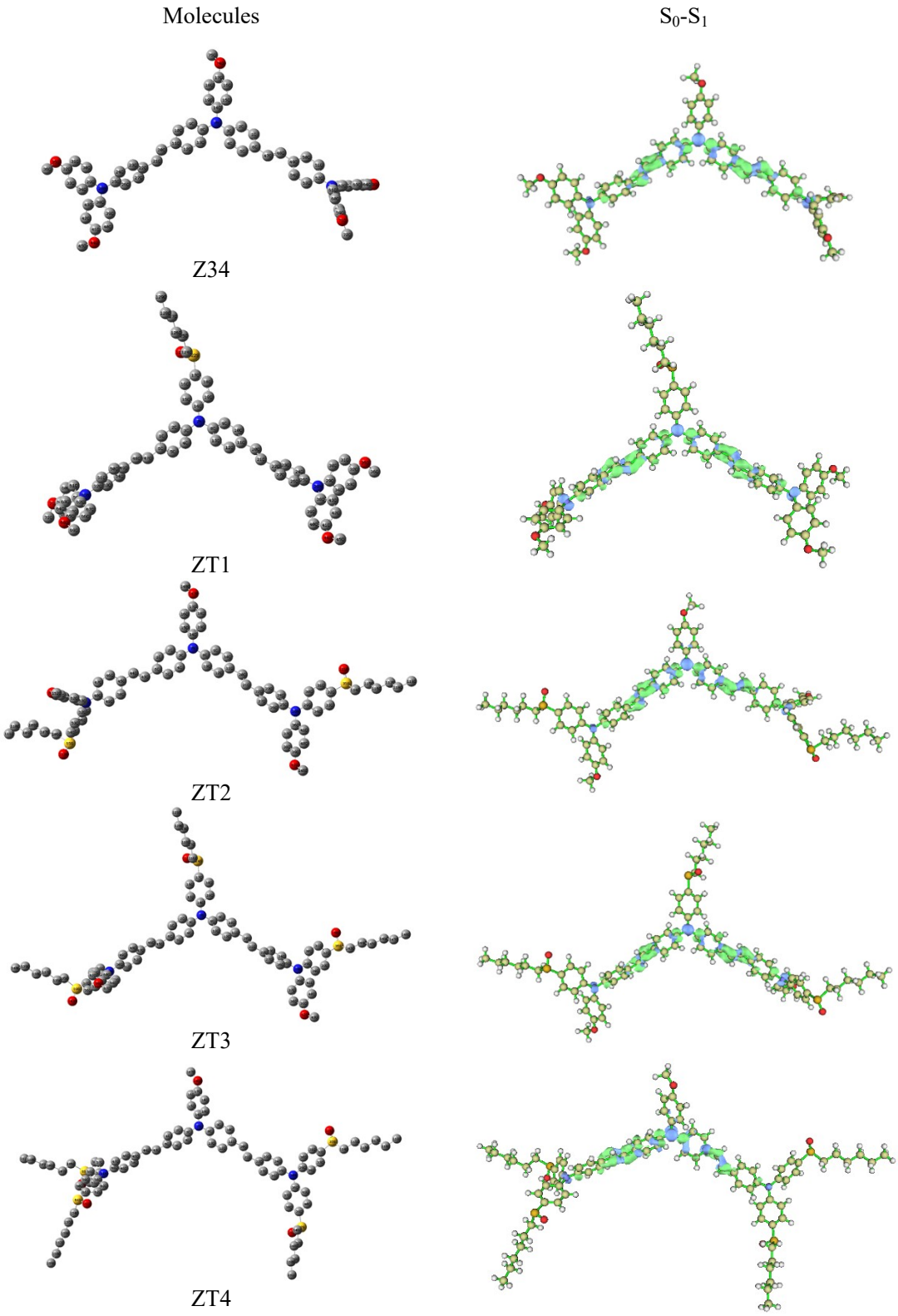

Fig.S3 The isosurface of hole and electron distribution simultaneously of Z34, ZT1, ZT2, ZT3 and ZT4, blue and green isosurfaces represent hole and electron distributions, respectively.

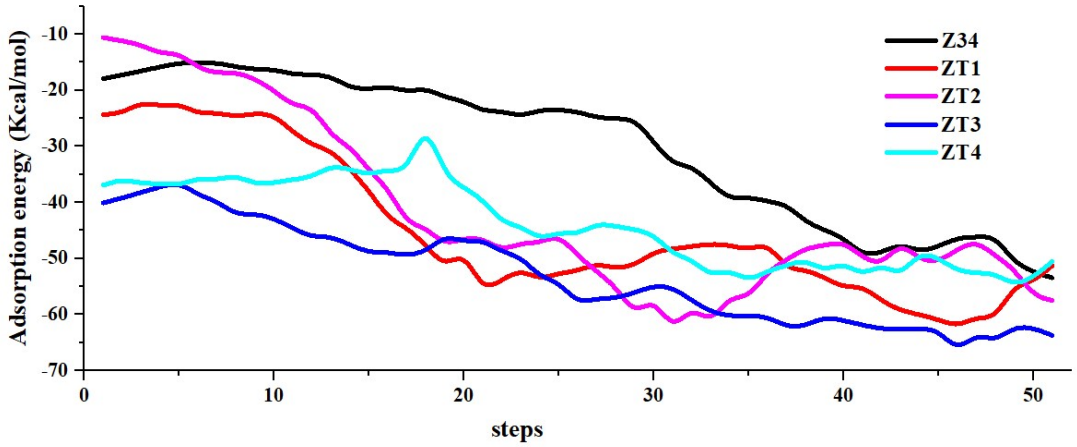

Fig. S4 The molecular dynamics (MD) simulations of ZT-based HTMs adsorbed on the PbI_2-terminated perovskite surface under the isothermal and isochoric ensemble (NVT) for 50 ps with a time step of 1 fs.