Table S1. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies calculated by six DFT functionals together with 6-31+G(d,p) basis set for molecule 4

functional	HOMO	exp[a]	LUMO	exp
B3LYP	-5.27	-5.10	-1.18	-2.90
PBE1PBE	-5.46		-1.01	
MPW1B95	-5.59		-0.78	
PBE33	-5.77		-0.75	
PBE38	-5.92		-0.62	
MPWB1K	-6.07		-0.38	

[a] ref 26.

Table S2 The absorption and fluorescence emission spectral data obtained in ethanol solvent by six TD-DFT functionals together with 6-31+G(d,p) basis set for molecule 4

functional	electronic transitions	$\lambda_{abs,max}$ (nm)	oscillator strength	λ_{exp} (nm)[b]	electronic transitions	λ_{em} (nm)
TD-B3LYP	$S_0 \rightarrow S_2$	302.71	0.32	387	$S_1 \rightarrow S_0$	383.34
TD-B3LYP[a]	$S_0 \rightarrow S_2$	303.97	0.27			
TD-PBE1PBE	$S_0 \rightarrow S_2$	294.80	0.31		$S_1 \rightarrow S_0$	372.37
TD-MPW1B95	$S_0 \rightarrow S_2$	291.35	0.34		$S_1 \rightarrow S_0$	365.06
TD-PBE33	$S_0 \rightarrow S_2$	286.09	0.36		$S_1 \rightarrow S_0$	356.96
TD-PBE38	$S_0 \rightarrow S_2$	282.45	0.38		$S_1 \rightarrow S_0$	350.09
TD-MPWB1K	$S_0 \rightarrow S_2$	279.98	0.40		$S_1 \rightarrow S_0$	343.51

[a] cc-pVTz basis set was used combined with TD-B3LYP.

[b] ref 28.

Table S3 Frequencies for optimized structures of studied molecules

1-1. Vibrational frequencies of 1.

14.790900 17.912400 30.543300 35.734900 55.680800 78.490900 106.694000 112.427800 120.879200 149.990000 150.342500 192.875100 235.717500 286.916100 293.376900 295.360400 304.841400 317.135300 335.755400 397.708900 409.056800 420.145000 433.299600 439.823700 454.402500 468.422700 534.518700 574.048700 584.922400 604.550600 629.415600 632.764000 730.417200 731.573000 735.193000 742.443000 749.440600 760.465700 765.424900 781.609500 792.805600 846.273800 854.936900 856.462100 858.853100 876.211200 927.511600 938.997700 940.648900 976.727300 978.291700 984.985800 1000.268100 1016.079200 1026.191900 1041.679600 1046.663600 1047.162500 1063.726500 1077.562000 1079.880900 1143.601700 1152.316700 1176.668100 1179.694700 1189.125600 1223.576800 1248.593800 1251.836400 1273.312000 1284.339300 1324.212900 1326.262800 1336.997000 1341.458500 1364.534000 1377.759400 1384.704600 1392.970600 1409.128200 1416.507000 1461.101000 1487.437700 1489.907400 1498.193200 1503.227200 1515.879200 1518.104200 1524.218900 1619.087200 1619.610700 1642.019300 1666.592000 3035.142100 3044.296700 3052.171100 3058.074100 3067.554900 3085.285700 3099.689100 3111.249100 3180.308900 3181.028900 3187.119500 3188.570800 3198.548000 3199.078000 3207.872700 3208.496000 3820.389500 3823.013600

1-2. Vibrational frequencies of 2.

12.848100 17.356400 24.221100 37.358100 43.031500 43.624300 55.617200 75.812200 99.132800 99.430000 112.680100 119.355900 122.672500 156.035000 203.718100 217.040000 239.440900 264.626100 304.493800 313.026500 316.138100 329.563800 332.233300 343.957600 365.139800 388.727600 409.043100 417.834500 432.161100 435.473400 453.490700 473.617100 482.689600 576.297800 589.137300 594.682300 607.233400 658.298400 697.713900 731.523800 731.808500 739.078100 756.228700 759.522600 778.776400 794.597800 805.176900 809.214400 849.939500 856.468800 878.206400 892.709600 896.945100 927.992400 930.882700 944.051400 944.714600 984.270700 1000.020100 1005.055500 1020.782000 1025.602300 1046.066000 1053.782900 1061.460700 1061.894400 1063.207400 1077.790800 1078.598600 1161.364900 1172.932000 1181.266500 1184.473300 1221.777500 1223.859000 1256.689200 1261.244200 1273.355800 1286.820600 1322.902500 1324.475100 1324.744800 1337.348400 1345.539200 1366.964700 1385.906500 1393.298100 1410.001100 1414.266400 1420.661400 1420.734500 1456.384800 1461.122500 1481.591600 1489.703200 1489.835600 1495.647800 1501.133800 1502.271600 1509.446800 1515.894200 1520.660800 1530.007300 1614.774200 1615.446900 1653.715900 1672.837100 3029.379800 3029.649200 3034.906600 3043.805900 3050.969200 3058.221400 3067.304800 3080.711100 3080.738200 3084.630500 3098.798200 3111.429600 3113.539400 3113.596400 3172.197000 3172.445200 3175.340300 3177.717300 3196.430900 3197.093200 3820.339900 3822.950700

1-3. Vibrational frequencies of 3.

13.372300 17.382200 20.177600 44.459600 55.263500 58.918800 72.478700 79.539700 94.396400 107.256400 112.372500 123.801800 129.802100 139.126300 198.744400 206.216600 213.095700 215.891700 261.069500 270.283400 278.028800 281.614600 305.134600 318.914800 335.370700 357.313800 358.711200 373.010500 409.030500 422.982000 432.856500 433.684300 447.454500 451.954000 470.746000 483.755000 517.070600 580.744500 599.533200 604.481100 629.591000 662.889400 698.175300 727.375300 732.063000 732.180700 757.412300 760.291900 763.037700 795.434800 812.006900 813.454100 850.617100 851.690600 855.993800 856.565800 878.689100 928.524900 938.150900 938.644200 942.281300 983.525900 999.475000 1024.901600 1037.934100 1045.473900 1054.110300 1063.112500 1068.999500 1078.827200 1088.446700 1149.435700 1164.041100 1172.246500 1172.347700 1182.178900 1190.163700 1205.338800 1224.919600 1226.544300 1237.791500 1268.954900 1273.696600 1273.986500 1297.709800 1322.647600 1323.647200 1326.506200 1338.920300 1349.740500 1368.766500 1394.931300 1400.202500 1411.571900 1413.129000 1461.545800 1468.896700 1469.664100 1476.684300 1494.960000 1495.064800 1495.836400 1501.335600 1506.057400 1509.814900 1511.782800 1516.254900 1518.545700 1527.223200 1616.708700 1621.077300 1652.244200 1671.976400 3007.562100 3008.044200 3034.863100 3043.645600 3050.726500 3058.646300 3067.066000 3067.224300 3067.226000 3084.303800 3098.472100 3111.838100 3145.922400 3146.020700 3193.229900 3193.789200 3213.423200 3213.570500 3216.595500 3218.138900 3820.391000 3823.008200

1-4. Vibrational frequencies of 4.

15.990900 22.815300 22.882600 55.466500 62.758300 80.714100 82.865300 91.958100 99.231000 120.815700 129.206100 159.351100 206.498300 217.824200 228.175400 260.977700 262.162400 280.365700 290.690800 309.086800 312.043100 336.602200 359.253000 366.423100 395.973200 409.460700 423.783300 434.056800 447.624100 452.574600 453.021100 483.858600 513.676700 575.118200 597.029800 604.399200 630.167300 662.118100 682.820500 725.227600 742.765000 745.535500 761.847700 762.364400 794.827600 813.368900 814.894400 848.675000 853.740300 859.587500 861.149500 888.357900 939.665600 940.113700 942.719300 983.076800 996.993000 1018.348700 1032.355200 1043.348100 1052.776700 1069.094000 1087.186700 1149.874300 1164.045900 1172.328600 1172.431100 1190.792800 1195.126800 1206.576100 1226.980100 1234.877000 1242.381400 1269.149800 1295.508900 1298.406000 1314.272200 1324.110700 1349.984100 1366.721100 1396.950700 1404.760600 1414.198200 1463.647800 1469.656600 1469.941500 1477.704400 1496.130000 1496.239600 1505.330200 1507.637000 1510.363700 1514.127500 1518.821300 1527.753900 1617.273100 1622.175900 1652.762200 1671.456800 3008.526300 3009.001500 3068.446200 3068.601800 3069.684800 3082.944300 3116.526500 3135.477000 3146.845000 3146.942300 3193.754300 3194.264000 3214.042700 3214.171000 3217.777200 3219.555200 3819.563400 3822.363100

1-5. Vibrational frequencies of 5.

19.661900 22.667200 24.243200 36.764200 45.865700 76.459700 77.537600

81.652600 85.828800 91.142700 122.117900 124.715500 135.914000 143.877300
171.298400 176.680100 183.718800 200.286900 228.010800 235.271100 254.872000
260.027700 262.388500 284.531000 290.673100 304.531500 313.136300 319.964500
326.577600 337.721700 383.836600 394.895400 403.067800 414.980300 421.818100
442.639200 451.536000 455.072900 464.838300 495.612400 530.688700 538.239600
552.675000 590.017000 625.703700 653.290000 658.800600 682.892400 700.848800
719.878700 739.903300 744.967900 753.935000 755.840500 758.805700 783.102800
784.085600 806.088300 818.998300 821.237200 859.544700 860.038100 864.644200
866.490200 881.731800 914.219200 965.774000 970.827400 983.902000 989.376600
999.365200 1031.046700 1035.001600 1045.271100 1072.980800 1078.281800
1105.420200 1134.291300 1170.033700 1171.499000 1173.347300 1177.070500
1198.738800 1204.399800 1206.828000 1216.087600 1232.820000 1237.967300
1244.133800 1261.230700 1263.984300 1288.107600 1298.570400 1301.148300
1319.358000 1351.705800 1362.359400 1378.363800 1395.509700 1404.480600
1420.372800 1441.039300 1447.597500 1459.012600 1463.906200 1480.480100
1482.620900 1486.784500 1495.631500 1497.027000 1499.716400 1503.148700
1506.258400 1508.847100 1512.452700 1514.589000 1525.852100 1539.830700
1614.351400 1622.038000 1644.656200 1658.549500 1670.463500 3009.463400
3013.188800 3054.529400 3069.503200 3070.260000 3075.856400 3083.276800
3116.463900 3129.980700 3135.657300 3149.062500 3152.408900 3158.988900
3178.087000 3192.401000 3199.610700 3218.809700 3224.580000 3230.252900
3817.868800 3820.995800

1-6. Vibrational frequencies of 6.

18.152000 24.558300 26.914400 44.651600 63.125000 67.628300 84.939400
97.082900 106.355400 126.716400 151.848300 161.443700 217.189900 235.235700
243.687200 267.796100 281.477800 304.388100 309.513000 320.685400 328.896700
335.380500 358.200800 391.111800 407.594700 412.468400 423.481500 448.694300
452.668300 467.525100 481.832200 509.101900 546.199200 560.228700 601.994900
611.448900 618.188100 646.106600 671.426100 715.574300 743.784700 745.286000
751.759000 758.245700 760.076600 765.647600 782.075200 792.145800 817.540900
842.507700 856.941800 860.850300 864.850300 871.768700 898.095100 913.087800
923.209200 940.572800 964.199700 983.297800 989.749600 996.922100
1005.236200 1032.554500 1038.461800 1042.598400 1054.558300 1080.260000
1150.452800 1158.585100 1172.802200 1178.860400 1186.846300 1190.373400
1211.547400 1233.787800 1236.794300 1246.472000 1255.588200 1286.893000
1293.939800 1298.660400 1317.481500 1341.727500 1373.710900 1384.546000
1397.245000 1405.178000 1407.082100 1442.839200 1464.042500 1465.568600
1477.511200 1495.143500 1496.094900 1506.669500 1513.775500 1514.235400
1521.616000 1541.603000 1619.232200 1626.960400 1656.829500 1663.224800
1676.881700 3010.341100 3070.141000 3070.842500 3084.308800 3117.427600
3136.708800 3148.601900 3171.042000 3174.609700 3179.320600 3188.603300
3190.666300 3196.333700 3203.883200 3214.753000 3220.522400 3819.110300
3822.012900

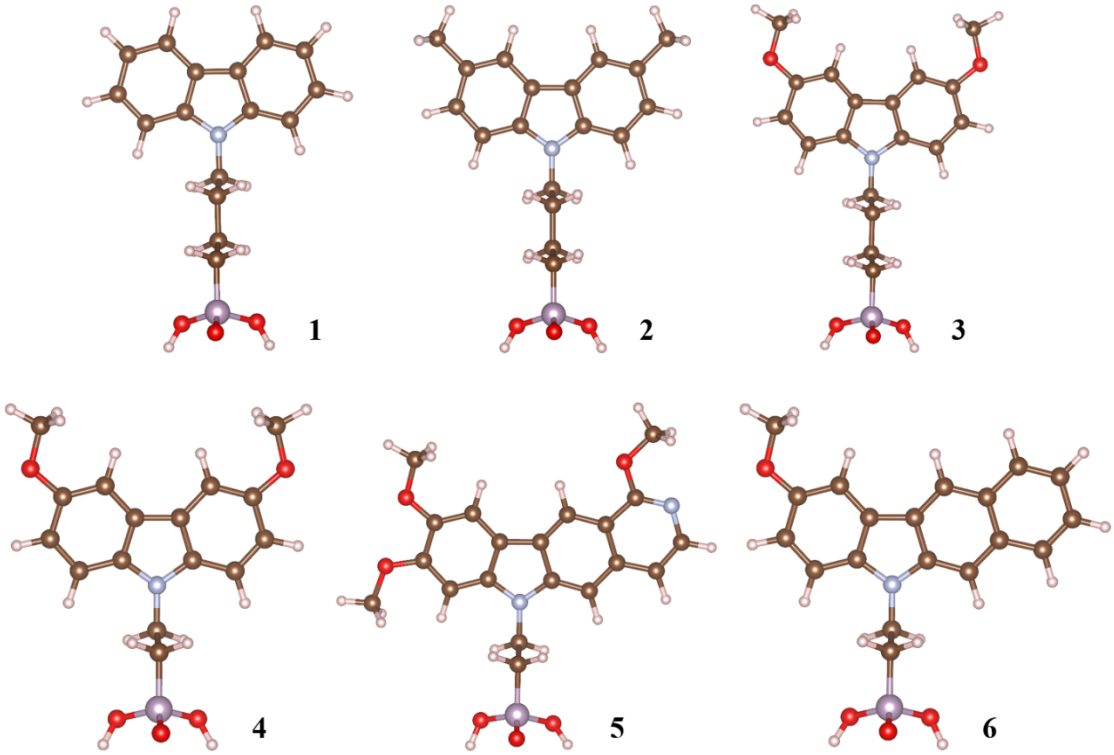
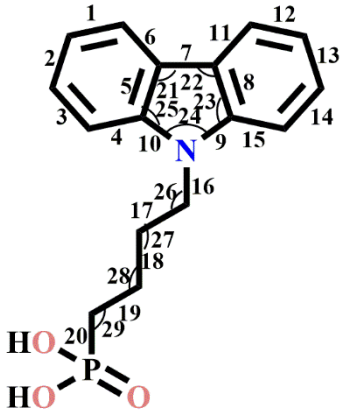
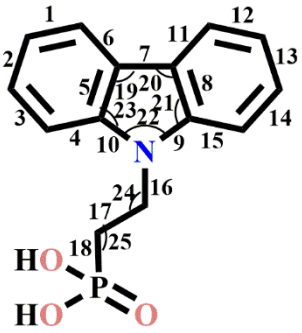


Figure S1. Optimized geometries of molecules 1-6.

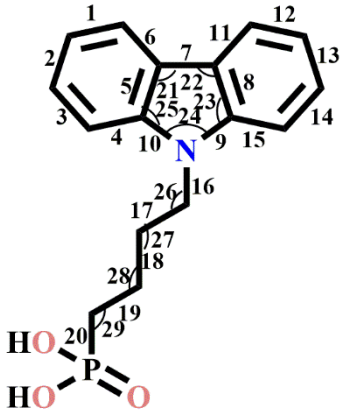
Table S4 Important bond lengths (Å) and bond angles (°) of molecules 1-6 in ground state geometry

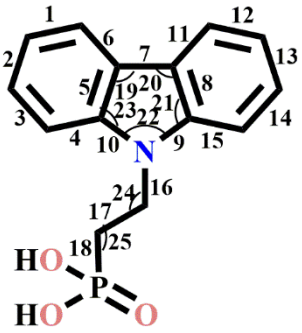




molecules	1	2	3	4	5	6
1	1.39	1.40	1.39	1.39	1.39	1.40
2	1.41	1.41	1.41	1.41	1.43	1.41
3	1.40	1.39	1.39	1.39	1.40	1.39
4	1.40	1.40	1.40	1.40	1.40	1.40
5	1.42	1.42	1.42	1.42	1.41	1.41
6	1.40	1.40	1.41	1.41	1.41	1.40
7	1.45	1.45	1.45	1.45	1.45	1.45
8	1.42	1.42	1.42	1.42	1.44	1.44
9	1.39	1.39	1.39	1.39	1.39	1.39
10	1.39	1.39	1.39	1.39	1.40	1.40
11	1.40	1.40	1.41	1.41	1.38	1.38
12	1.39	1.40	1.39	1.39	1.41	1.42
13	1.41	1.41	1.41	1.41	1.43	1.44
14	1.40	1.39	1.39	1.39	1.42	1.42
15	1.40	1.40	1.40	1.40	1.38	1.38
16	1.45	1.45	1.45	1.45	1.45	1.45
17	1.54	1.54	1.54	1.55	1.55	1.55
18	1.53	1.53	1.53	1.81	1.81	1.81
19	1.54	1.54	1.54	106.6	106.9	106.7
20	1.81	1.81	1.81	106.6	106.5	106.5
21	106.6	106.6	106.6	109.3	108.5	108.6
22	106.6	106.6	106.6	108.2	108.6	108.6
23	109.1	109.3	109.3	109.3	109.5	109.5
24	108.6	108.3	108.1	112.4	112.4	112.2
25	109.1	109.3	109.3	114.8	114.8	114.8
26	113.6	113.6	113.7			
27	112.1	112.1	112.1			
28	111.9	111.8	111.9			
29	115.5	115.5	115.5			

Table S5 Important bond lengths (Å) and bond angles (°) of molecules 1-6 in singlet excited state geometry





molecules	1	2	3	4	5	6
1	1.42	1.42	1.42	1.42	1.41	1.41
2	1.40	1.40	1.41	1.41	1.45	1.42
3	1.43	1.42	1.42	1.42	1.39	1.39
4	1.39	1.39	1.39	1.39	1.41	1.40
5	1.43	1.43	1.43	1.43	1.45	1.45
6	1.41	1.41	1.41	1.41	1.39	1.39
7	1.44	1.44	1.44	1.44	1.45	1.44
8	1.43	1.43	1.43	1.43	1.40	1.41
9	1.40	1.40	1.39	1.39	1.43	1.42
10	1.40	1.40	1.39	1.39	1.36	1.37
11	1.41	1.41	1.41	1.41	1.41	1.41
12	1.42	1.42	1.42	1.42	1.42	1.42
13	1.40	1.40	1.41	1.41	1.44	1.45
14	1.43	1.42	1.42	1.42	1.43	1.44
15	1.39	1.39	1.39	1.39	1.39	1.38
16	1.45	1.45	1.45	1.45	1.45	1.45
17	1.54	1.54	1.54	1.54	1.54	1.54
18	1.53	1.53	1.53	1.81	1.81	1.81
19	1.54	1.54	1.54	107.3	107.3	107.2
20	1.81	1.81	1.81	107.3	106.7	106.9
21	107.4	107.3	107.3	107.5	108.6	108.2
22	107.4	107.3	107.3	110.4	109.6	109.8
23	107.5	107.7	107.6	107.5	107.9	107.9
24	110.2	110.1	110.3	111.2	111.5	111.4
25	107.5	107.7	107.6	114.4	114.4	114.3
26	112.2	112.3	112.4			
27	111.6	111.6	111.8			
28	111.5	111.5	111.6			
29	115.3	115.3	115.4			

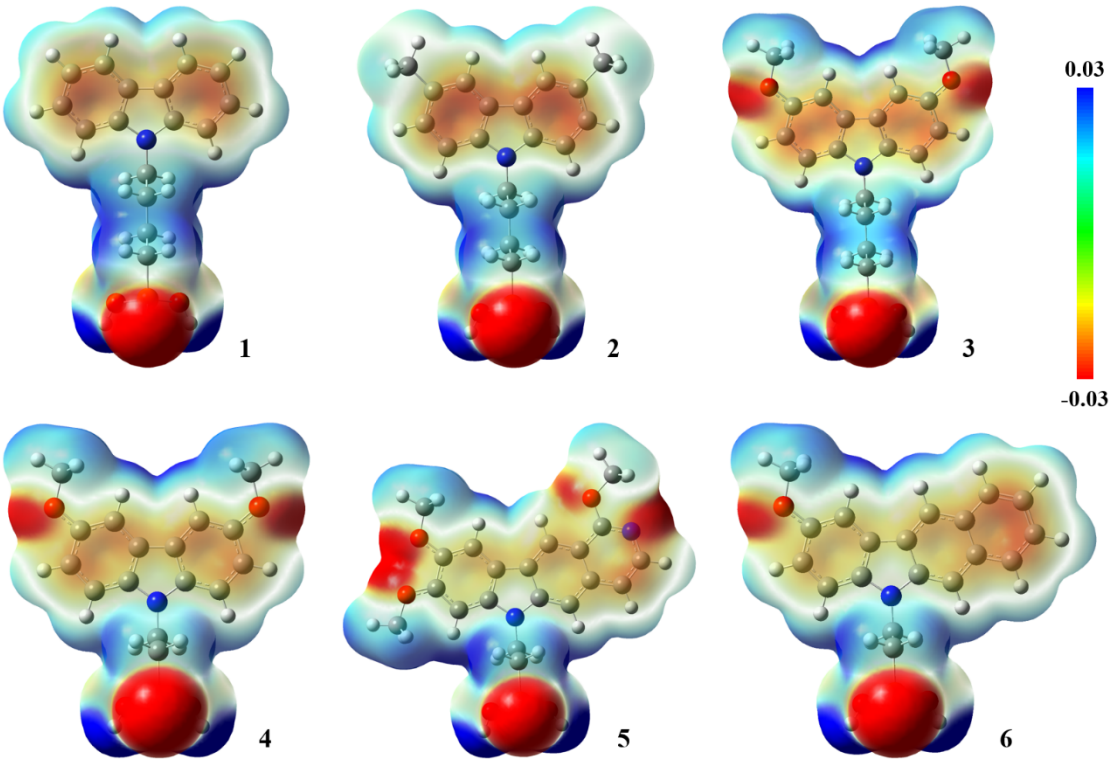


Figure S2. ESP mapped onto a surface of electron distribution for the studied compounds.

Table S6 Centroid-to-centroid distance [d (Å)], hole reorganization energy [λ_{hole} (eV)], hole transfer integral [V_{hole} (eV)], hole hopping rate constant [k_{hole} (s^{-1})], and hole mobility [μ_{hole} ($cm^2V^{-1}s^{-1}$)] for the molecules 1-6

molecules	path	d	λ_{hole}	V_{hole}	k_{hole}	μ_{hole}
1	2	10.30	0.11	5.71×10^{-3}	5.68×10^{11}	0.12
	3	8.38		4.65×10^{-3}	3.77×10^{11}	0.05
	4	10.01		6.99×10^{-3}	8.52×10^{11}	0.17
	5	12.16		3.90×10^{-3}	2.65×10^{11}	0.08
2	2	9.20	0.16	9.68×10^{-3}	8.35×10^{11}	0.14
	3	9.58		7.77×10^{-3}	5.38×10^{11}	0.10
	4	8.38		5.23×10^{-3}	2.44×10^{11}	0.03
	5	9.36		7.93×10^{-3}	5.60×10^{11}	0.09
	6	10.71		9.32×10^{-3}	7.74×10^{11}	0.17
3	2	8.77	0.27	6.43×10^{-3}	9.79×10^{10}	0.01
	3	9.71		8.99×10^{-3}	1.91×10^{11}	0.03
	4	7.90		6.37×10^{-3}	9.61×10^{10}	0.01
	5	8.50		6.05×10^{-3}	8.67×10^{10}	0.01
	6	9.99		6.73×10^{-3}	1.07×10^{11}	0.02
4	2	5.33	0.30	1.03×10^{-2}	1.78×10^{11}	0.01
	3	8.38		5.01×10^{-3}	4.22×10^{10}	0.01
	4	7.37		7.52×10^{-3}	9.50×10^{10}	0.01
	5	8.05		6.22×10^{-3}	6.50×10^{10}	0.01
5	2	5.83	0.33	8.31×10^{-3}	8.28×10^{10}	0.01
	3	4.75		4.76×10^{-2}	2.72×10^{12}	0.12
	4	9.01		7.22×10^{-3}	6.25×10^{10}	0.01
	5	9.70		6.61×10^{-3}	5.24×10^{10}	0.01
6	2	9.32	0.21	2.29×10^{-3}	2.52×10^{10}	0.004
	3	9.08		3.23×10^{-3}	5.00×10^{10}	0.01
	4	4.67		6.84×10^{-3}	2.24×10^{11}	0.01

	5	9.13	4.03×10^{-3}	7.79×10^{10}	0.01

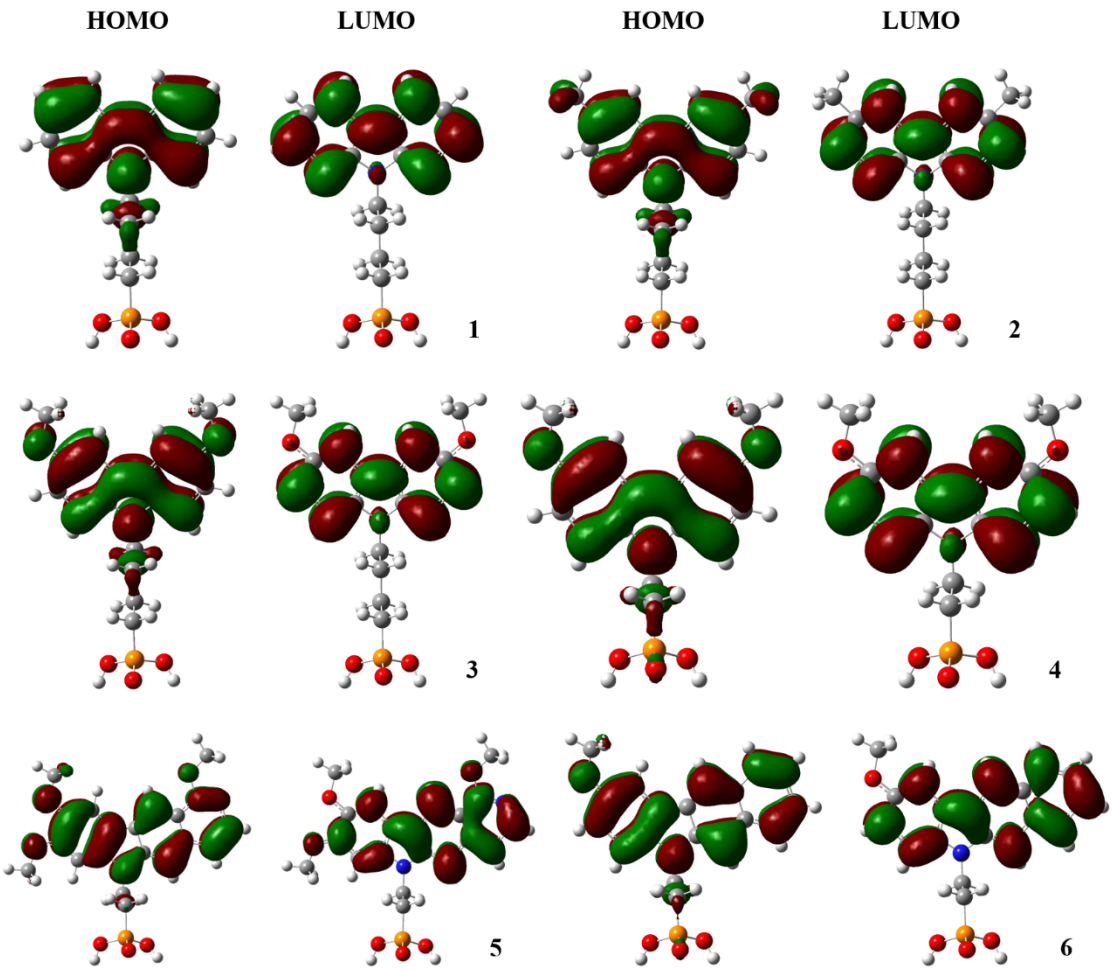


Figure S3. Spatial distribution of HOMOs and LUMOs for molecules 1-6.

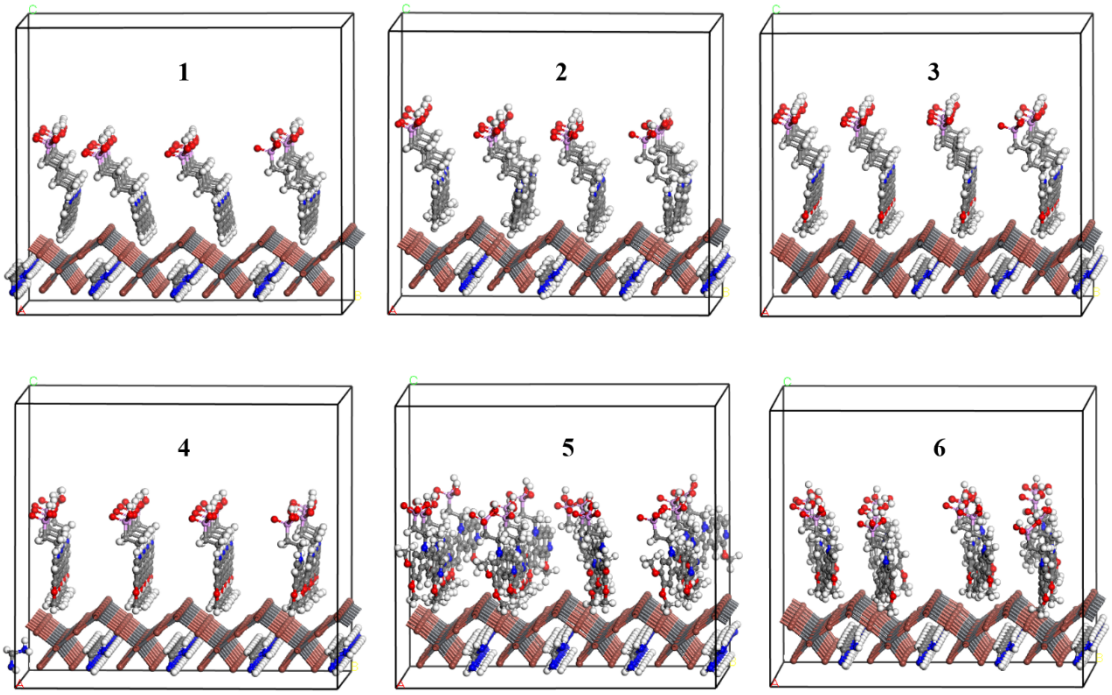


Fig. S4 Optimized geometry of each HTSAM adsorbed on $FAPbI_3$ surface.

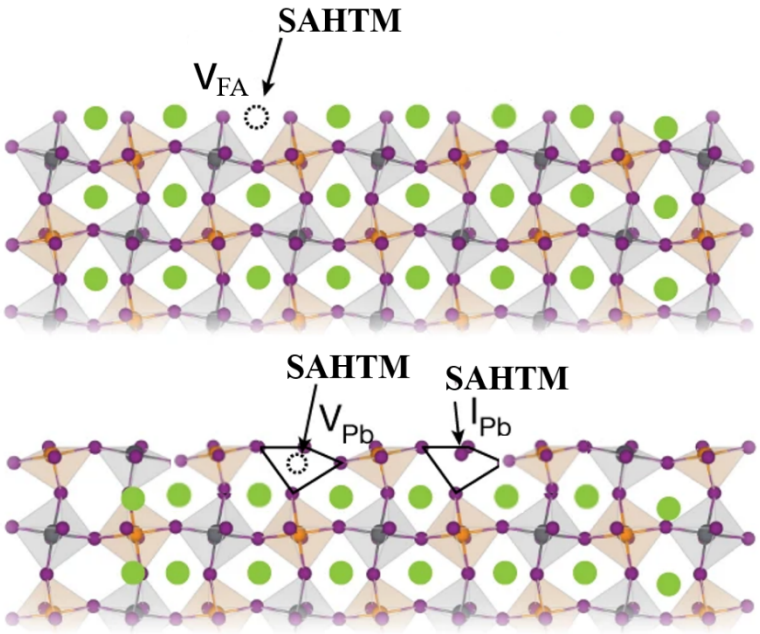


Fig. S5 Schematic diagram of the interaction between SAHTM with the acceptor-like defects, *i.e.*, formamidinium (FA) vacancy (V_{FA}), Pb vacancy (V_{Pb}) and I_{Pb} vacancy.