Supporting Information:

Nature of Fluorine Interactions in 'Wheel and Axle' Topology Based Hexa-Coordinated Sn(IV)-Porphyrins: An Experimental and Theoretical Analysis.

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Synthesis and Experimental Section

Materials. Reagents and solvents were purchased from commercial sources and purified by standard procedures before use. Grade-I basic alumina was used for column chromatography. $Sn(TpyP)(OH)_2$[1] were prepared by literature methods.

Preparation of $[Sn(T^4PyP)(L)_2]$[L = 3-Fluorobenzoic acid]:

trans-Dihydroxo[5,10,15,20-tetrakis(4-pyridyl)porphyrinato]tin(IV) (7.7 mg, 0.01 mmol) and 3-Fluorobenzoic acid (3.15 mg, 0.025 mmol) was placed in a sealed reactor with 5 mL of $CHCl_3$ and 0.5 mL of DMF. The mixture was heated for 1 hour at 70 C, and after cooling to room temperature. Reaction mixture was poured into a test tube put for slow evaporation. After 7 days, fine pink crystals of complex were obtained, Yield (7.9 mg, 78%). FT-IR (KBr, cm^{-1}) 1707, 1442, 1207, 1031, 785, 761, 660, 575, 449. UV-Vis in DCM: λmax/nm (log e) 420(5.48), 553(2.98), 591(2.15).

Preparation of [Sn(T4PyP)(L)2][L = 4-Fluorobenzoic acid]:

trans-Dihydroxo[5,10,15,20-tetrakis(4-pyridyl)porphyrinato]tin(IV) (7.7 mg, 0.01 mmol) and 4-Fluorobenzoic acid (3.15 mg, 0.025 mmol) was placed in a sealed reactor with 5

mL of $CHCl_3$ and 0.5 mL of DMF. The mixture was heated for 1 hour at 70 ^{0}C, and after cooling to room temperature. Reaction mixture was poured into a test tube and put for slow evaporation. After 7 days, X-ray quality small thin plate pink crystals of complex were obtained, Yield (8.5 mg, 84%). FT-IR (KBr, cm^{-1}) 1701, 1441, 1212, 1032, 785, 760, 660, 575, 448. UV-Vis in DCM: λmax/nm (log e) 421(5.44), 554(3.12).591(2.12)

Preparation of [Sn(T4PyP)(L)2][L = 3,5-Difluorobenzoic acid]:

trans-Dihydroxo[5,10,15,20-tetrakis(4-pyridyl)porphyrinato]tin(IV) (7.7 mg, 0.01 mmol) and 3,5-difluorobenzoic acid (3.59 mg, 0.025 mmol) was placed in a sealed reactor with 5 mL of $CHCl_3$ and 0.5 mL of CH_3OH. The mixture was heated for 1 hour at 70 ^{0}C, and after cooling to room temperature. Reaction mixture was poured into a test tube and layered with methanol, put for slow evaporation. After 6 days fine pink crystals of complex were obtained, Yield (8.3 mg, 79%). FT-IR (KBr, cm^{-1}) 3092, 1660, 1407, 1213, 1031, 780, 748, 661, 573, 487. UV-Vis in DCM: $\lambda_{max/nm}$ (log e) 420(5.64), 553(3.25). 591(2.16)

Preparation of [Sn(T4PyP)(L)2][L = 2,3,4,5,6-Pentafluorobenzoic acid]:

trans-Dihydroxo[5,10,15,20-tetrakis(4-pyridyl)porphyrinato]tin(IV) (7.7 mg, 0.01 mmol) and 2,3,4,5.6-Pentafluorobenzoic acid (4.77 mg, 0.025 mmol) was placed in a sealed reactor with 5 mL of $CHCl_3$ and 0.5 mL of CH_3OH. The mixture was heated for 1 hour at 70 ^{0}C, and after cooling to room temperature. Reaction mixture was poured into a test tube and layered with diethylether, put for slow evaporation. After 7 days, X-ray quality small thin plate pink crystal of complex were obtained, Yield (8.2 mg, 78%). FT-IR (KBr, cm^{-1}) 3068, 1679, 1408, 1252, 1032, 802, 741, 660, 571, 519. UV-Vis in DCM: λmax/nm (log e) 418(5.68), 552(3.32), 590(2.24)

Instrumentation

Absorption spectra were recorded on Perkin-Elmer Lambda 35. The FT-IR spectra were recorded from KBr pellets in the 4000–400 cm^{-1} range on a Nicolet 5DX spectrometer.

Single crystal X-ray diffraction: Single-crystal X-ray diffraction data for compound **1 2** and **4** were collected with 'SuperNova Diffractometer' equipped with HyPix3000 detector from Rigaku Oxford Diffraction. Data collection and reduction were performed with inbuilt program suite (CrysAlisPro 1.171.39.33c (Rigaku OD, 2017)) and an absorption correction (multi-scan method) was also done. Structures were solved by the direct method using SHELXS-97 and were refined on F^2 by full-matrix least-squares technique using the SHELXL-2018/3[2] program package on WINGX[3] platform. All non hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at their stereo-chemical positions and were riding with their respective non-hydrogen atoms with SHELXL default parameters.

Diffraction data for compound-**3** were collected with BRUKER SMART APEX CCD Diffractometer equipped with low-temperature apparatus (CRYO Industries). Data collection and reduction were performed with inbuilt BRUKER-APEX and SAINT programs.[4] Absorption correction was performed with SADABS program.[5] Structure solution and further refinements were performed as described above.

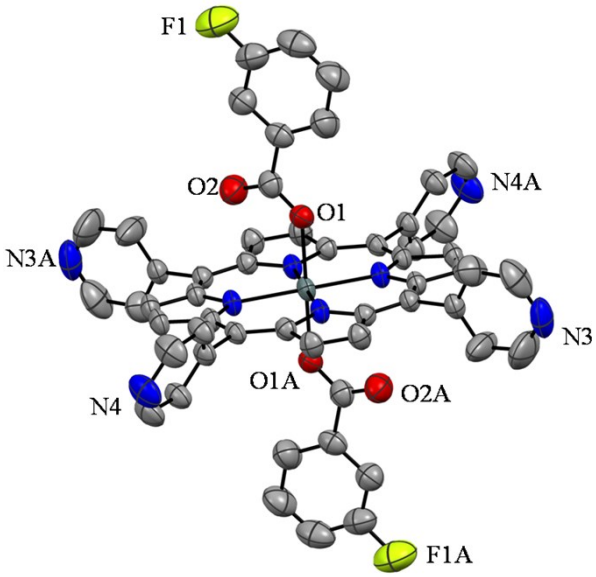

Figure S1. Perspective view of compound **1** showing 50% thermal contours for all non-hydrogen atoms at 293 K (H-atoms have been omitted for clarity).

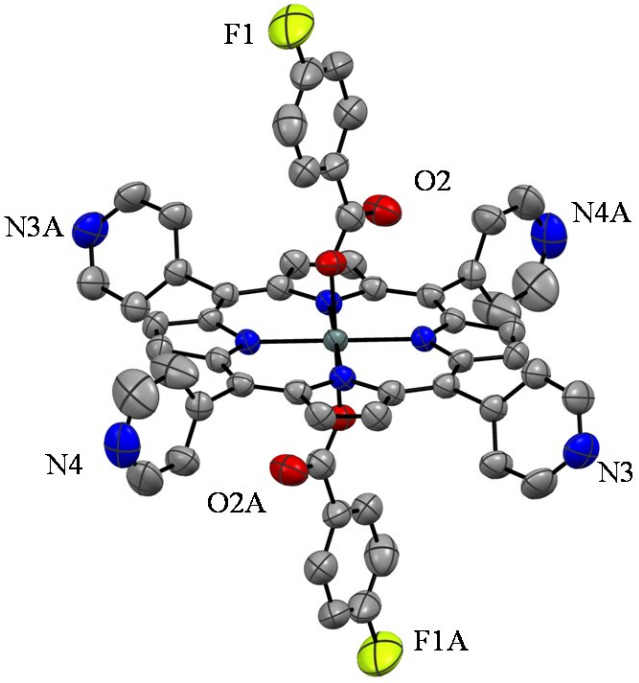

Figure S2. Perspective view of compound **2** showing 50% thermal contours for all non-hydrogen atoms at 293 K (H-atoms have been omitted for clarity).

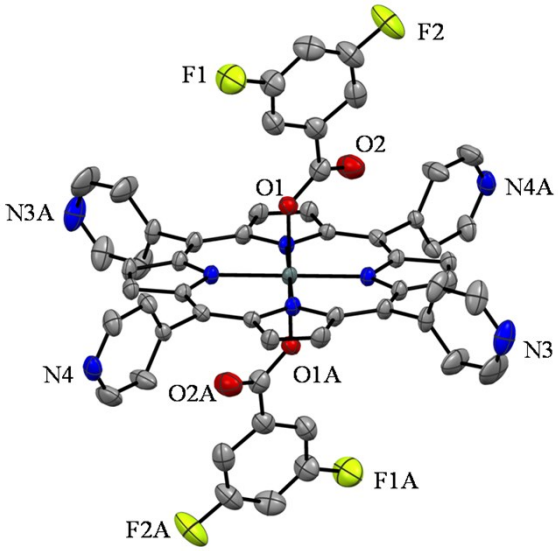

Figure S3. Perspective view of compound **3** showing 50% thermal contours for all non-hydrogen atoms at 100 K (H-atoms have been omitted for clarity).

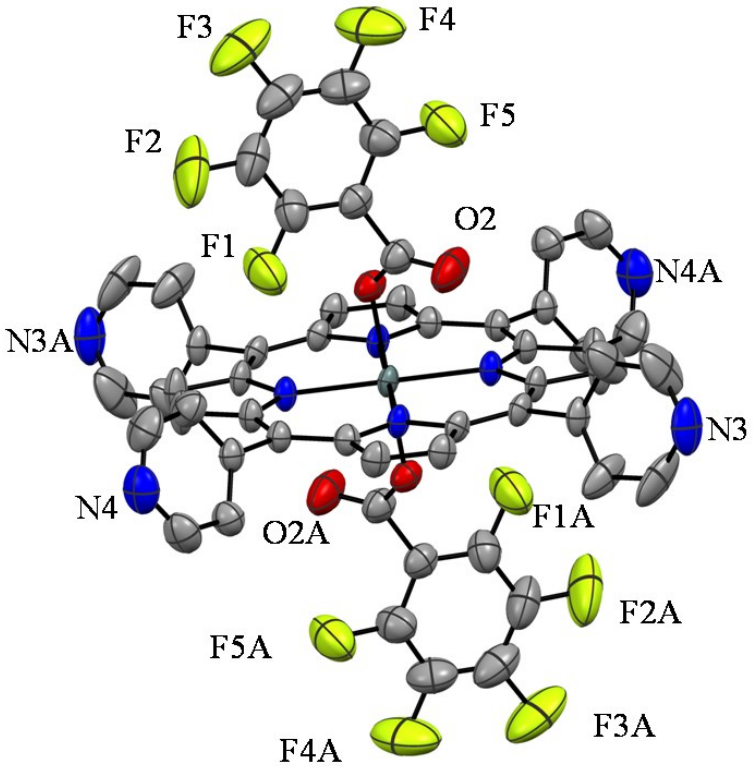

Figure S4. Perspective view of compound**4** showing 50% thermal contours for all non-hydrogen atoms at 293 K (H-atoms have been omitted for clarity).

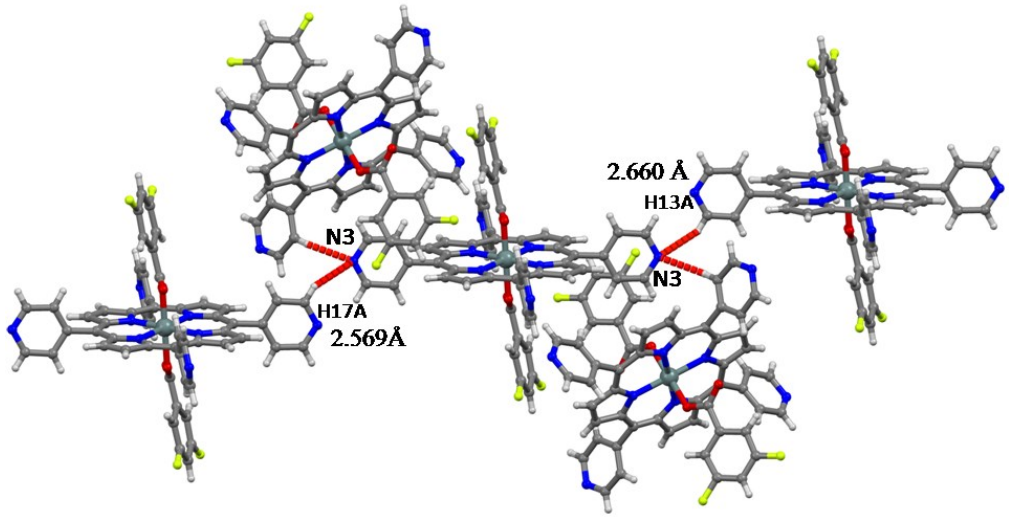

Figure S5. Bifurcated hydrogen bonding interactions in **3.** N3 is simultaneously involved in hydrogen bonding with H13A and H17A

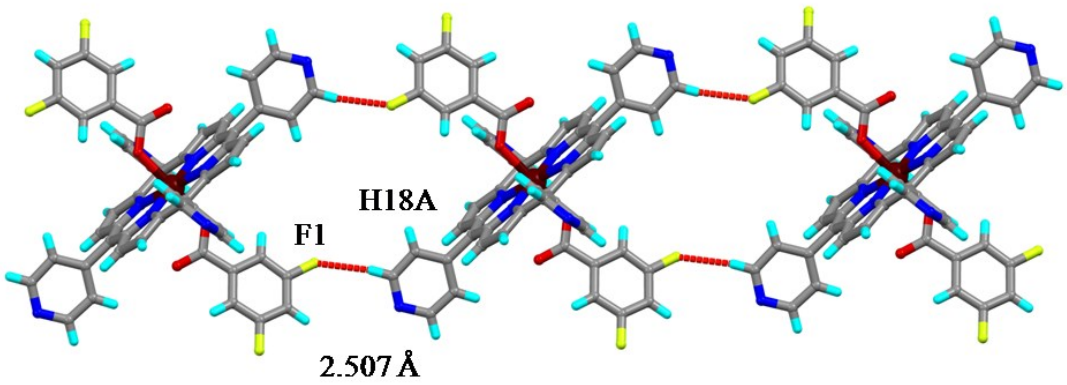

Figure S6. Hydrogen bonding interactions in **3** where F1 is hydrogen bonding with pyridyl proton (H18A) of porphyrin.

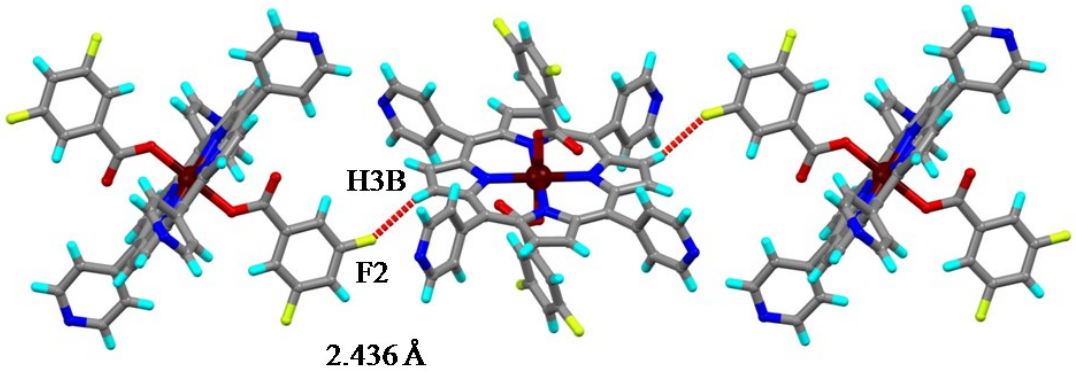

Figure S7. Hydrogen bonding interactions in **3** where F2 is hydrogen bonding with *β*-pyrrole proton (H3B) of porphyrin.

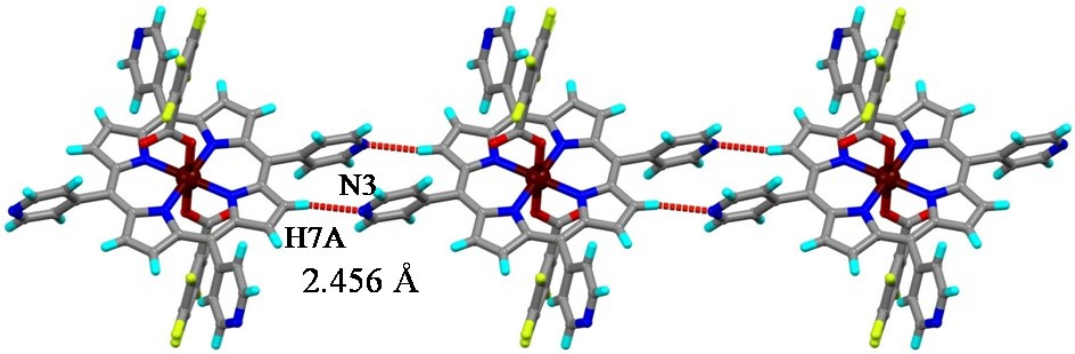

Figure S8. Hydrogen bonding interactions in **4** where N4 is hydrogen bonding with *β*-pyrrole proton (H7A) of porphyrin.

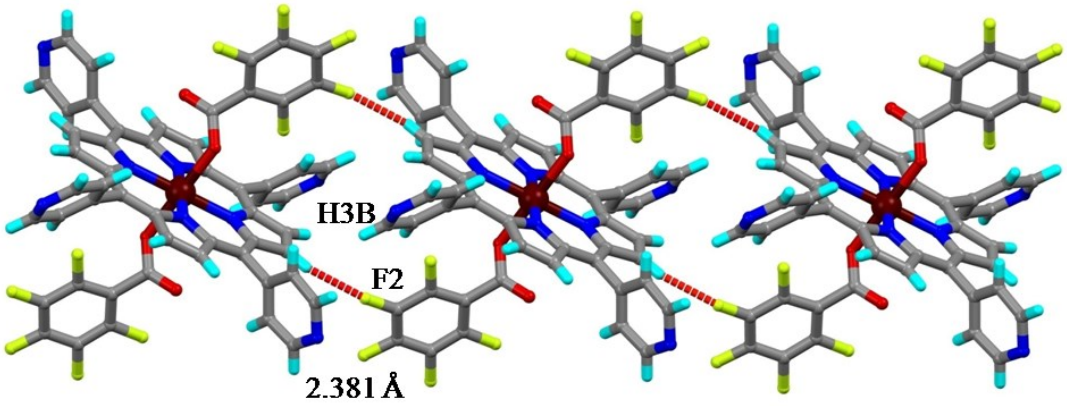

Figure S9. Hydrogen bonding interaction in **4** where F2 is hydrogen bonding with *β*-pyrrole proton (H3B) of porphyrin

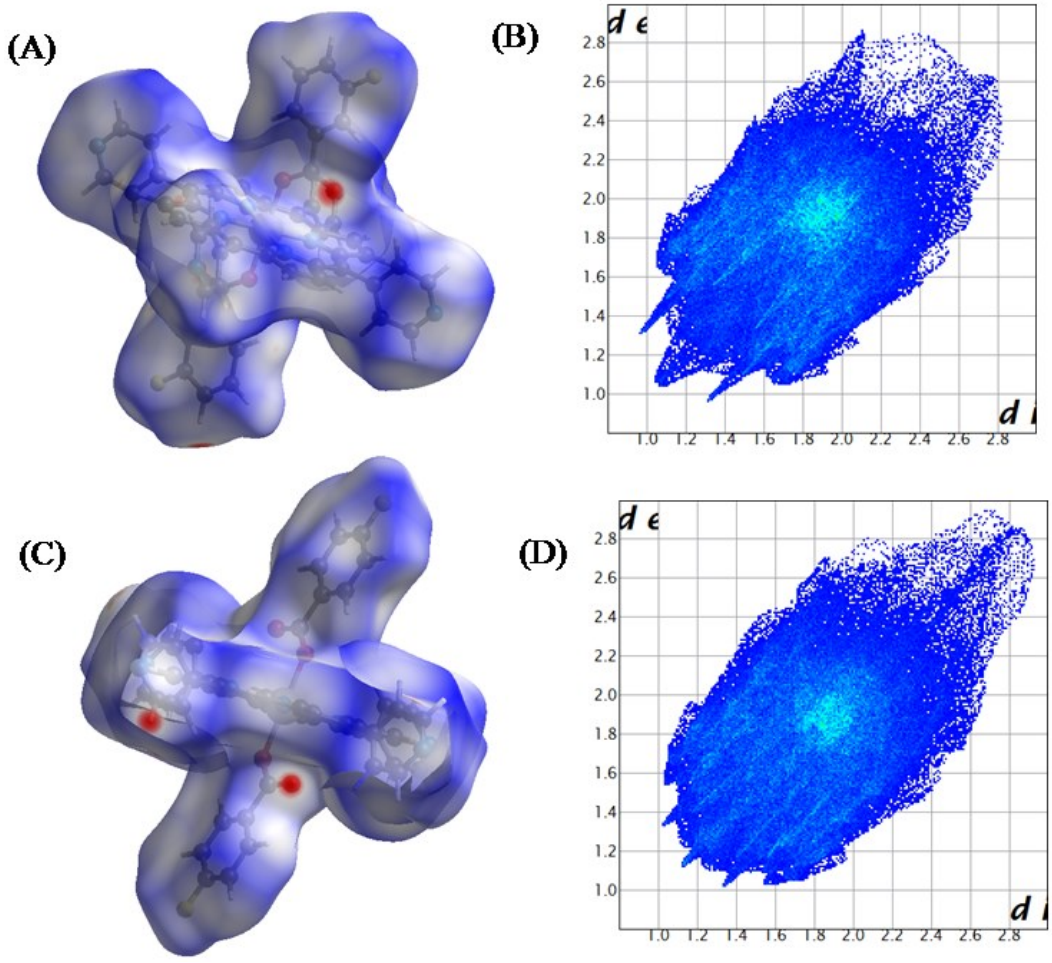

Figure S10. Calculated Hirschfield surfaces of **1** (A) and **2** (C) and the fingerprint plots of **1** (B) and **2** (D)

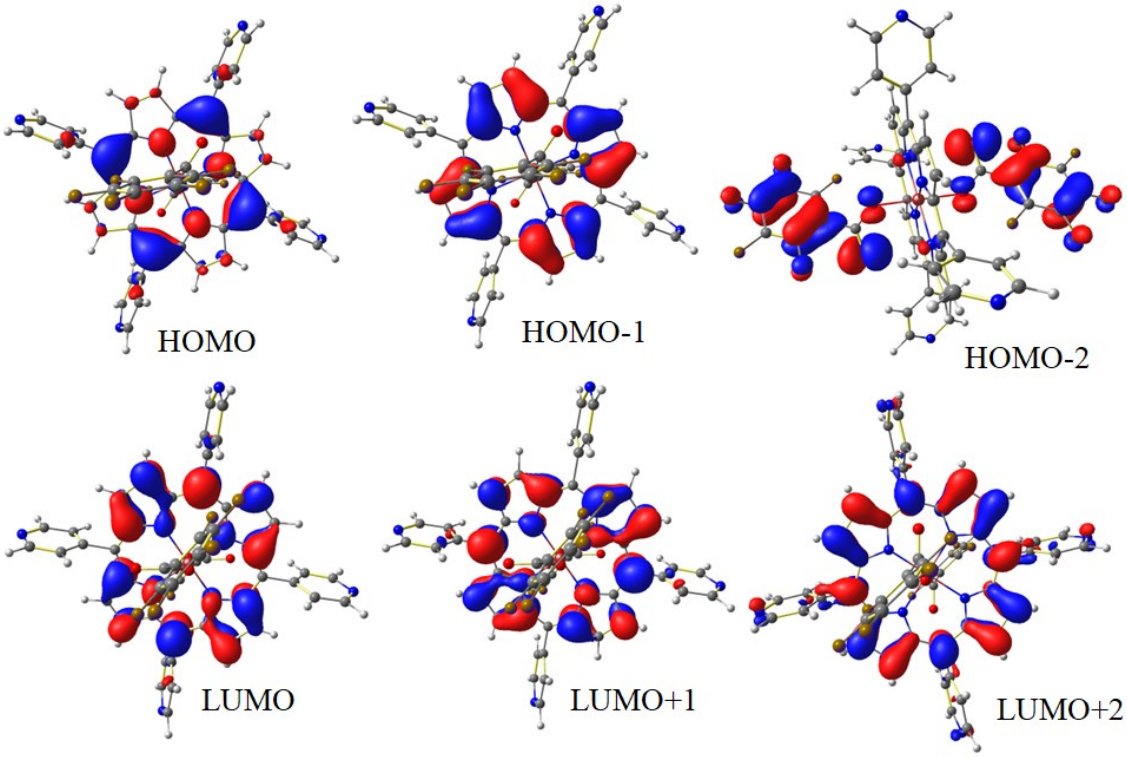

Figure S11. Different HOMO and LUMO label for the compound **4**, computational level: B3LYP/6-31G*(d,p)

Computational Details:

DFT calculations have been carried out by employing a B3LYP hybrid functional using, Gaussian 09, revision B.05, package.[6] Dispersion correction was done during optimization of the geometry. Using the method of Becke's three-parameter hybrid exchange functional,[7] the nonlocal correlation provided by the Lee, Yang, and Parr expression,[8] and Vosko, Wilk, and Nussair 1980 correlation functional (III) for local correction. The basis set was LANL2DZ for the Sn-atom and 6-31G** for C, N, O, F and H-atom. The coordinates are taken directly from the single-crystal X-ray data. Geometry optimization of **3** and **4** [Sn(TpyP)$(L)_2$; L= 3,5-difluoro benzoic acid] and Sn(TpyP)$(L)_2$; L= 2,3,4,5,6-pentafluoro benzoic acid] were performed. Molecular electrostatic potential surfaces were calculated from optimized geometry.

Table S1. Coordinates of optimized geometry of **3**

Sn	8.549282000	9.855786000	8.460375000
F	15.312979000	8.929799000	7.859391000
F	14.115546000	4.645631000	6.323860000

N	9.345129000	11.493292000	7.425569000
N	7.655329000	9.189075000	6.688852000
N	8.281028000	12.413825000	1.088583000
N	4.560591000	3.510016000	6.399123000
O	10.339990000	8.922500000	8.073119000
O	9.726600000	6.869694000	7.341384000
C	10.090330000	12.503541000	7.989540000
C	10.392546000	13.466682000	6.961085000
H	10.959929000	14.373608000	7.110007000
C	9.824884000	13.024285000	5.801907000
H	9.843451000	13.508016000	4.836632000
C	9.161185000	11.776166000	6.090446000
C	8.426725000	10.998304000	5.169998000
C	7.737915000	9.800593000	5.457853000
C	7.020974000	8.987798000	4.505613000
H	6.919039000	9.209316000	3.453659000
C	6.521422000	7.910342000	5.177356000
H	5.934969000	7.098721000	4.772436000
C	6.925025000	8.030452000	6.555510000
C	6.623571000	7.112977000	7.580240000
C	8.375462000	11.488767000	3.755696000
C	7.189833000	11.985886000	3.198162000
H	6.279739000	12.033819000	3.788473000
C	7.198095000	12.431265000	1.875325000
H	6.287179000	12.825224000	1.427520000
C	9.410829000	11.937008000	1.625452000
H	10.282801000	11.924447000	0.973533000
C	9.512115000	11.468766000	2.936387000
H	10.456294000	11.085844000	3.311863000
C	5.889216000	5.870469000	7.174962000
C	4.506325000	5.732650000	7.337834000
H	3.914171000	6.536885000	7.764690000
C	3.897889000	4.541385000	6.935972000
H	2.822762000	4.412398000	7.050994000
C	5.884346000	3.650269000	6.248588000
H	6.408446000	2.801127000	5.812935000
C	6.592334000	4.795830000	6.615299000

H	7.668019000	4.860791000	6.480835000
C	10.576378000	7.711591000	7.615933000
C	12.044719000	7.408977000	7.440441000
C	13.025561000	8.358962000	7.749093000
H	12.750169000	9.336648000	8.123196000
C	14.359794000	8.020740000	7.564686000
C	14.757905000	6.776968000	7.085859000
H	15.804768000	6.533080000	6.948968000
C	13.754895000	5.858516000	6.789841000
C	12.407727000	6.146608000	6.956762000
H	11.644811000	5.415149000	6.719856000
N	7.753432000	8.218283000	9.495182000
N	9.443238000	10.522496000	10.231897000
N	8.817533000	7.297749000	15.832167000
N	12.537958000	16.201564000	10.521635000
C	7.008228000	7.208036000	8.931212000
C	6.706009000	6.244896000	9.959669000
H	6.138624000	5.337972000	9.810747000
C	7.273674000	6.687293000	11.118845000
H	7.255106000	6.203562000	12.084120000
C	7.937376000	7.935410000	10.830305000
C	8.671838000	8.713269000	11.750752000
C	9.360650000	9.910979000	11.462896000
C	10.077593000	10.723772000	12.415137000
H	10.179528000	10.502254000	13.467090000
C	10.577144000	11.801229000	11.743394000
H	11.163596000	12.612850000	12.148315000
C	10.173538000	11.681121000	10.365241000
C	10.474988000	12.598600000	9.340512000
C	8.723100000	8.222807000	13.165055000
C	9.908728000	7.725686000	13.722588000
H	10.818823000	7.677750000	13.132276000
C	9.900466000	7.280307000	15.045425000
H	10.811381000	6.886346000	15.493229000
C	7.687733000	7.774569000	15.295299000
H	6.815762000	7.787132000	15.947218000
C	7.586448000	8.242811000	13.984363000

H	6.642270000	8.625735000	13.608888000
C	11.209340000	13.841109000	9.745792000
C	12.592229000	13.978934000	9.582914000
H	13.184384000	13.174704000	9.156052000
C	13.200661000	15.170200000	9.984777000
H	14.275788000	15.299193000	9.869751000
C	11.214204000	16.061305000	10.672176000
H	10.690103000	16.910443000	11.107836000
C	10.506220000	14.915742000	10.305464000
H	9.430535000	14.850775000	10.439934000
F	1.785591000	10.781773000	9.061442000
F	2.983019000	15.066185000	10.596296000
O	6.758576000	10.789078000	8.847624000
O	7.371964000	12.841994000	9.579048000
C	6.522190000	12.000026000	9.304706000
C	5.053849000	12.302666000	9.480148000
C	4.073007000	11.352632000	9.171646000
H	4.348401000	10.374887000	8.797697000
C	2.738775000	11.690880000	9.356002000
C	2.340662000	12.934727000	9.834633000
H	1.293799000	13.178635000	9.971488000
C	3.343670000	13.853227000	10.130505000
C	4.690839000	13.565111000	9.963627000
H	5.453754000	14.296609000	10.200418000

Table S2. Coordinates of optimized geometry of **4**

Sn	4.955283000	9.063868000	5.420875000
O	5.945033000	10.854987000	5.699031000
N	3.194692000	10.058596000	4.886660000
N	4.444875000	9.255567000	7.440089000
O	5.563676000	12.037647000	3.799687000
N	-0.729591000	12.663081000	9.351220000
C	1.274078000	11.279752000	7.926532000
C	2.816738000	10.382024000	3.601306000
C	2.949175000	10.574205000	1.136286000
C	3.516426000	10.058303000	2.423037000
C	1.603519000	11.155328000	3.672209000

H	1.074188000	11.554738000	2.819828000
C	2.285282000	10.613084000	5.762983000
C	3.345504000	9.920127000	7.934414000
C	2.346980000	10.556798000	7.170243000
C	5.179127000	8.776288000	8.499925000
F	5.677342000	15.008431000	8.785775000
N	1.909843000	11.588444000	-1.279835000
C	1.280652000	11.299054000	4.990489000
H	0.439424000	11.834427000	5.405317000
C	3.383652000	9.843629000	9.373755000
H	2.644683000	10.268842000	10.036515000
C	6.406751000	13.159385000	5.717148000
C	-0.028070000	10.774088000	8.023449000
H	-0.291861000	9.830209000	7.555643000
F	8.744150000	15.937566000	5.307457000
C	4.503605000	9.145321000	9.718430000
H	4.846784000	8.903485000	10.713446000
C	5.924491000	11.934805000	4.961570000
C	6.242372000	14.677599000	7.617330000
C	1.846024000	9.976854000	0.515311000
H	1.369779000	9.103264000	0.950780000
C	-0.981488000	11.498504000	8.741481000
H	-1.998537000	11.120406000	8.832379000
C	5.854343000	13.521307000	6.946975000
C	7.221798000	15.496233000	7.059805000
C	1.545876000	12.498810000	8.562315000
H	2.537501000	12.937522000	8.508505000
C	7.376920000	14.004367000	5.174231000
C	0.517348000	13.141389000	9.253208000
H	0.706195000	14.090939000	9.751334000
C	1.371990000	10.519029000	-0.681105000
H	0.517555000	10.068072000	-1.183450000
C	3.518140000	11.695142000	0.517435000
H	4.365507000	12.198807000	0.973112000
C	7.795437000	15.156584000	5.836435000
C	2.963392000	12.155656000	-0.677667000
H	3.386279000	13.027104000	-1.174838000

F	4.891185000	12.769981000	7.511611000
F	7.958742000	13.707070000	4.007011000
F	7.609262000	16.604572000	7.696025000
N	6.715880000	8.069144000	5.955088000
N	5.465695000	8.872168000	3.401660000
N	10.640245000	5.464773000	1.490531000
C	8.636525000	6.848031000	2.915217000
C	7.093840000	7.745725000	7.240442000
C	6.961410000	7.553551000	9.705463000
C	6.394151000	8.069444000	8.418711000
C	8.307064000	6.972429000	7.169540000
H	8.836401000	6.573027000	8.021920000
C	7.625296000	7.514666000	5.078766000
C	6.565069000	8.207614000	2.907335000
C	7.563599000	7.570951000	3.671505000
C	4.731447000	9.351453000	2.341823000
N	8.000758000	6.539330000	12.121584000
C	8.629936000	6.828710000	5.851260000
H	9.471172000	6.293350000	5.436431000
C	6.526925000	8.284115000	1.467994000
H	7.265898000	7.858908000	0.805235000
C	9.938661000	7.353731000	2.818316000
H	10.202422000	8.297612000	3.286136000
C	5.406969000	8.982418000	1.123318000
H	5.063793000	9.224257000	0.128301000
C	8.064551000	8.150921000	10.326438000
H	8.540782000	9.024518000	9.890968000
C	10.892105000	6.629348000	2.100286000
H	11.909145000	7.007475000	2.009402000
C	8.364766000	5.628974000	2.279418000
H	7.373153000	5.190233000	2.333212000
C	9.393318000	4.986431000	1.588526000
H	9.204500000	4.036882000	1.090386000
C	8.538594000	7.608753000	11.522854000
H	9.393021000	8.059725000	12.025198000
C	6.392463000	6.432606000	10.324314000
H	5.545104000	5.928926000	9.868636000

C	6.947218000	5.972100000	11.519416000
H	6.524347000	5.100646000	12.016586000
O	3.965517000	7.272756000	5.142722000
O	4.346758000	6.090159000	7.042129000
F	4.233349000	3.119318000	2.056060000
C	3.503796000	4.968361000	5.124653000
F	1.166484000	2.190103000	5.534307000
C	3.985989000	6.192968000	5.880228000
C	3.668278000	3.450137000	3.224489000
C	4.056247000	4.606450000	3.894844000
C	2.688867000	2.631472000	3.781995000
C	2.533641000	4.123352000	5.667552000
C	2.115183000	2.971114000	5.005347000
F	5.019381000	5.357817000	3.330223000
F	1.951778000	4.420640000	6.834753000
F	2.301458000	1.523115000	3.145775000

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