

Electronic Supplementary Information

Stabilization of Unusual Diorganotin Carboxylates Using Intramolecular Coordination

Approach: Synthesis, Structure, TD-DFT, and Hirshfeld Surface Analyses

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Instrumentation

^1H , ^{13}C and ^{119}Sn NMR spectra were recorded in CDCl_3 solution on a Bruker Ascend 500MHz WB NMR spectrometer operating at 500 MHz. The chemical shifts are referenced with respect to tetramethylsilane (for ^1H & ^{13}C) and $\text{nBu}_2\text{SnCl}_2$ (for ^{119}Sn). Absorption spectra was recorded on Varian spectrophotometer Cary 4000 as a reference with path length of 1cm. TGA was recorded on TGA-6000 thermal analyser (Perkin Elmer) from 50 to 600°C. FTIR spectra was recorded on a Bruker Vertex 70V Infrared Fourier vacuum spectrometer using KBr pellet. The HRMS data were collected using a 6545 LC/Q-TOF HRMS. Elemental analyses were performed on Elementar elemental analyzer. Small deviation in the elemental analysis in this case is attributed to the solvated nature of the organometallic complex and elemental analysis results are in close agreement for unsolvated complex and is provided in the synthesis part.

X-ray crystallography

Single crystal X-ray crystallography: Suitable crystals for single crystal X-ray diffractions were loaded on a Bruker AXS Smart Apex CCD diffractometer. All the structures were solved by direct methods using SHELXS-97^{S1} and refined by full-matrix least squares on F^2 using SHELXL-97^{S2}. The details pertaining to the data collection and refinement for **1-5** are given in Table S1-S2. Non-hydrogen atoms were refined with anisotropic displacement parameters. All the hydrogen atoms were included in idealized positions and their positions were refined isotropically by a riding model. In case of Complex **2**, as the solvent molecules were disordered with high thermal factor values even at 100 K, squeeze analysis was performed using Program PLATON^{S3} and squeeze results were appended in the CIF file. The solvent (methanol) has been squeezed here due to disorder. The number of electrons per unit cell was found to 166 and the number of atoms per unit cell i.e $Z = 4$. Overall, there are 41 electrons per asymmetric unit, which is almost equivalent to 2 methanol molecules are asymmetric unit. Also, in this case, one of the benzene ring is disordered (C43 TO C48) over two position. Only for the higher

fraction (C43A to C48A with occupancy 0.6), anisotropic refinement is used whereas the lower fraction fraction (C43B to C48V with occupancy 0.4), is refined isotropically. Due to twinning in the crystal, it is scaled using twinabs. In case of Complex **5**, one of the lattice chloroform was found to be disordered over two positions and modeled using part command. The major fractions (Cl4A to Cl6A) were modeled with 0.8 occupancies and refined anisotropically whereas the minor fractions (Cl4B to Cl6B) have 0.2 occupancies and refined isotropically.

Table S1. Crystal data and structure refinement for complexes 1-3.

Identification code	1	2	3
Empirical formula	C ₃₁ H ₂₁ N ₅ O ₄ Sn	C ₅₅ H ₄₆ N ₁₀ O ₇ Sn ₂	C ₃₄ H ₂₉ ClN ₄ O ₅ Sn
Formula weight	646.22	1196.436	727.75
Temperature/K	298(2)	100(2)	298(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c
a/Å	12.485(7)	11.9525(12)	8.0541(15)
b/Å	15.878(8)	23.158(2)	17.145(3)
c/Å	14.951(8)	18.547(2)	23.719(4)
α/°	90	90	90
β/°	113.157(6)	96.271(3)	90.277(3)
γ/°	90	90	90
Volume/Å ³	2725(2)	5103.1(9)	3275.2(10)
Z	4	4	4
ρ _{calc} /g/cm ³	1.575	1.557	1.476
μ/mm ⁻¹	0.985	1.036	0.908
F(000)	1296.0	2264.0	1472.0
Crystal size/mm ³	0.393 × 0.341 × 0.298	0.280 × 0.190 × 0.140	0.250 × 0.190 × 0.120
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	3.548 to 49.998	4.624 to 50	2.93 to 49.998
Index ranges	-14 ≤ h ≤ 14, -18 ≤ k ≤ 18, -17 ≤ l ≤ 17	-14 ≤ h ≤ 14, -27 ≤ k ≤ 27, -22 ≤ l ≤ 22	-9 ≤ h ≤ 9, -20 ≤ k ≤ 20, -28 ≤ l ≤ 28
Reflections collected	34575	8947	42382
Independent reflections	4788 [R _{int} = 0.0243,	8947 [R _{int} = 0.0,	5765 [R _{int} = 0.0727,

	$R_{\text{sigma}} = 0.0139]$	$R_{\text{sigma}} = 0.0640]$	$R_{\text{sigma}} = 0.0470]$
Data/restraints/parameters	4788/0/370	8947/18/649	5765/0/409
Goodness-of-fit on F^2	1.051	1.100	1.090
Final R indexes [$I \geq 2\sigma$ (I)]	$R_1 = 0.0180, wR_2 = 0.0444$	$R_1 = 0.0766, wR_2 = 0.1513$	$R_1 = 0.0437, wR_2 = 0.1113$
Final R indexes [all data]	$R_1 = 0.0212, wR_2 = 0.0469$	$R_1 = 0.1028, wR_2 = 0.1644$	$R_1 = 0.0606, wR_2 = 0.1248$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.26/-0.2	1.14/-1.63	1.46/-0.62

Table S2. Crystal data and structure refinement for complexes 4-5.

Identification code	4	5
Empirical formula	$C_{70}H_{62}Cl_6N_8O_{12}Sn_2$	$C_{80}H_{58}Cl_{12}N_{10}O_{10}Sn_2$
Formula weight	1657.38	1982.14
Temperature/K	298(2)	100(2)
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	11.341(2)	13.1022(13)
b/Å	12.832(3)	13.2926(14)
c/Å	13.512(3)	13.3483(13)
$\alpha/^\circ$	114.565(2)	105.191(3)
$\beta/^\circ$	95.928(2)	94.932(3)
$\gamma/^\circ$	110.400(2)	113.326(3)
Volume/Å ³	1603.6(5)	2012.4(4)
Z	1	1
$\rho_{\text{calc}}/\text{g/cm}^3$	1.469	1.636
μ/mm^{-1}	0.847	1.085
F(000)	720.0	992.0
Crystal size/mm ³	0.230 × 0.180 × 0.120	0.293 × 0.245 × 0.211
Radiation	MoK α ($\lambda = 0.71073$)	MoK α ($\lambda = 0.71073$)
2 Θ range for data collection/ $^\circ$	3.464 to 49.996	5.506 to 50
Index ranges	$-13 \leq h \leq 13, -15 \leq k \leq 15, -16 \leq l \leq 16$	$-15 \leq h \leq 15, -15 \leq k \leq 15, -15 \leq l \leq 15$
Reflections collected	28811	24215
Independent reflections	5631 [$R_{\text{int}} = 0.0247, R_{\text{sigma}} = 0.0175$]	7077 [$R_{\text{int}} = 0.0405, R_{\text{sigma}} = 0.0415$]

Data/restraints/parameters	5631/0/419	7077/0/527
Goodness-of-fit on F^2	1.039	1.085
Final R indexes [$I > 2\sigma(I)$]	$R_1 = 0.0203$, $wR_2 = 0.0503$	$R_1 = 0.0323$, $wR_2 = 0.0701$
Final R indexes [all data]	$R_1 = 0.0231$, $wR_2 = 0.0528$	$R_1 = 0.0392$, $wR_2 = 0.0747$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.36/-0.26	1.05/-0.71

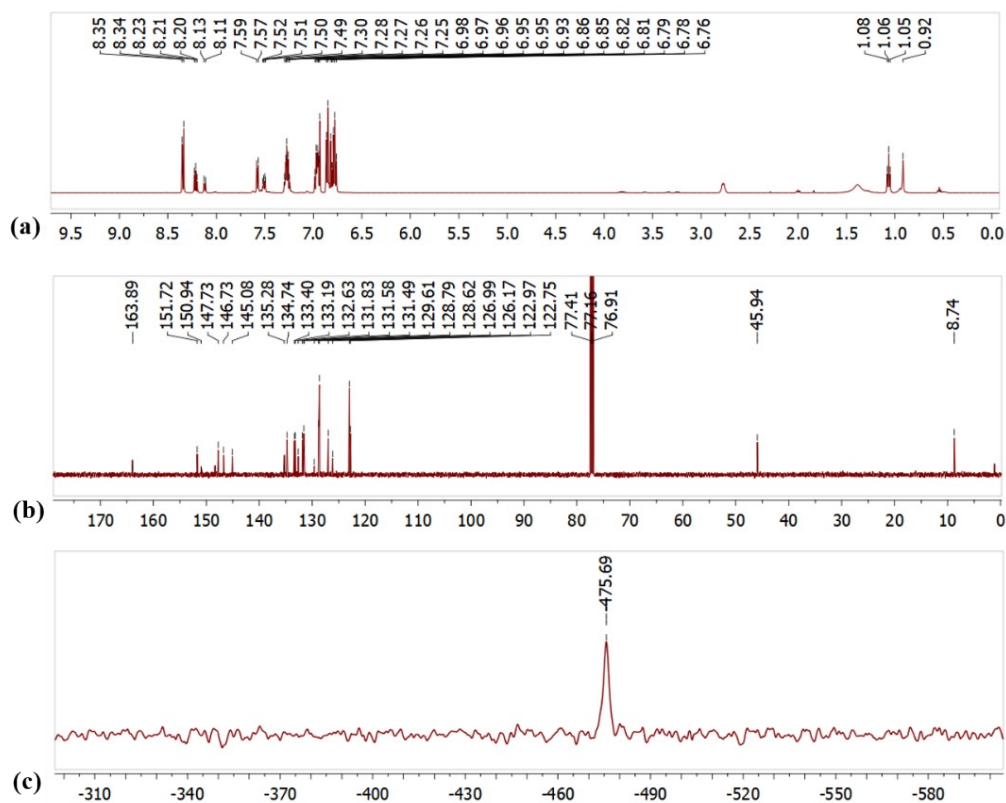


Figure S1. (a) ^1H NMR, (b) ^{13}C NMR and (c) ^{119}Sn NMR spectrum of complex **1** recorded in CDCl_3 .

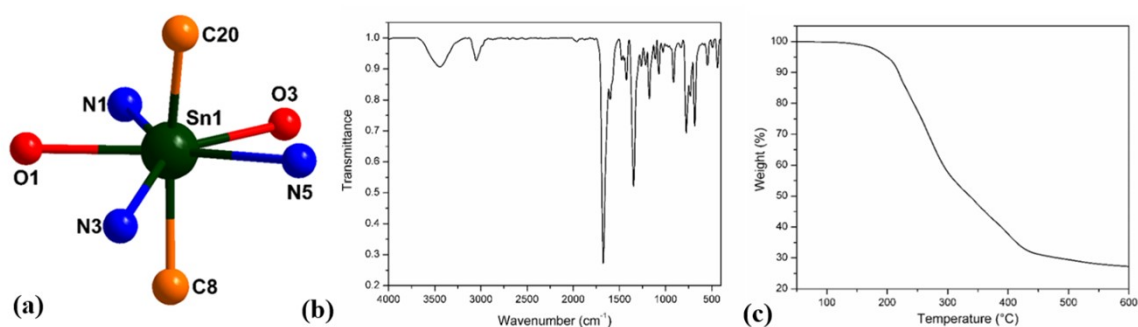


Figure S2. (a) Coordination environment of Sn center in **1**, (b) FTIR spectrum, (c) TGA plot, (d) ESI-MS spectrum of complex **1**.

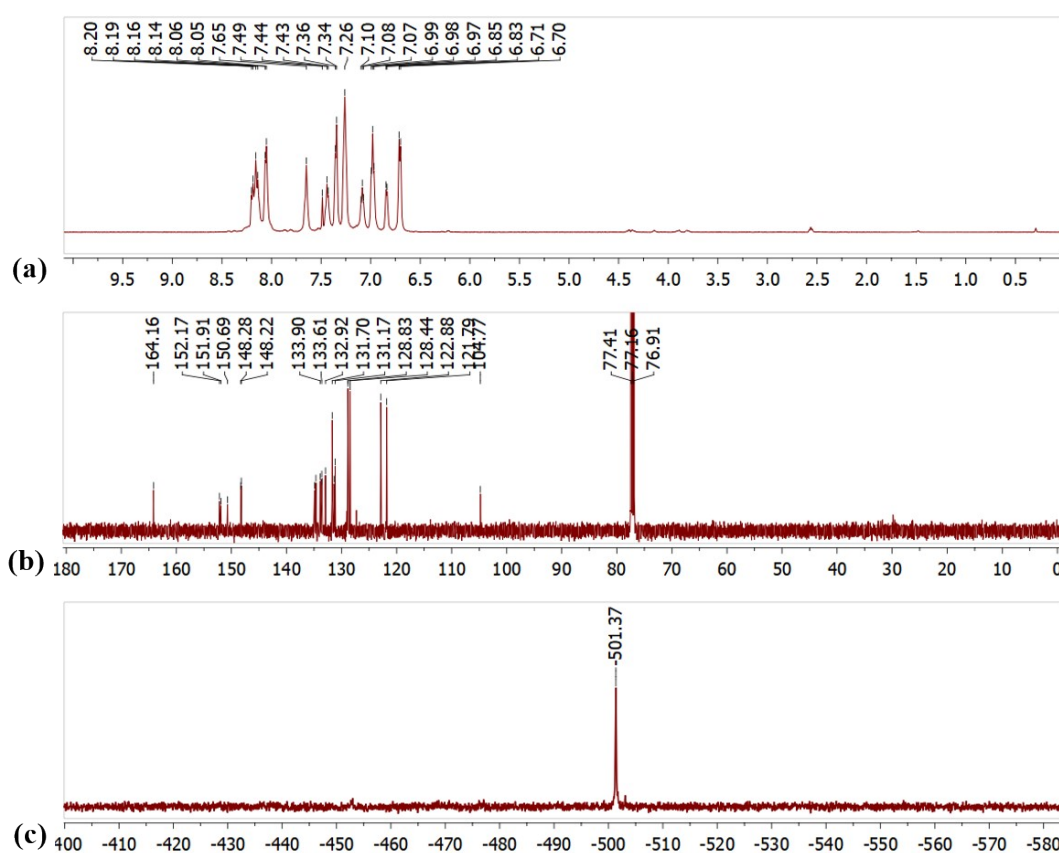


Figure S3. (a) ¹H NMR, (b) ¹³C NMR and (c) ¹¹⁹Sn NMR spectrum of complex **2** recorded in CDCl₃.

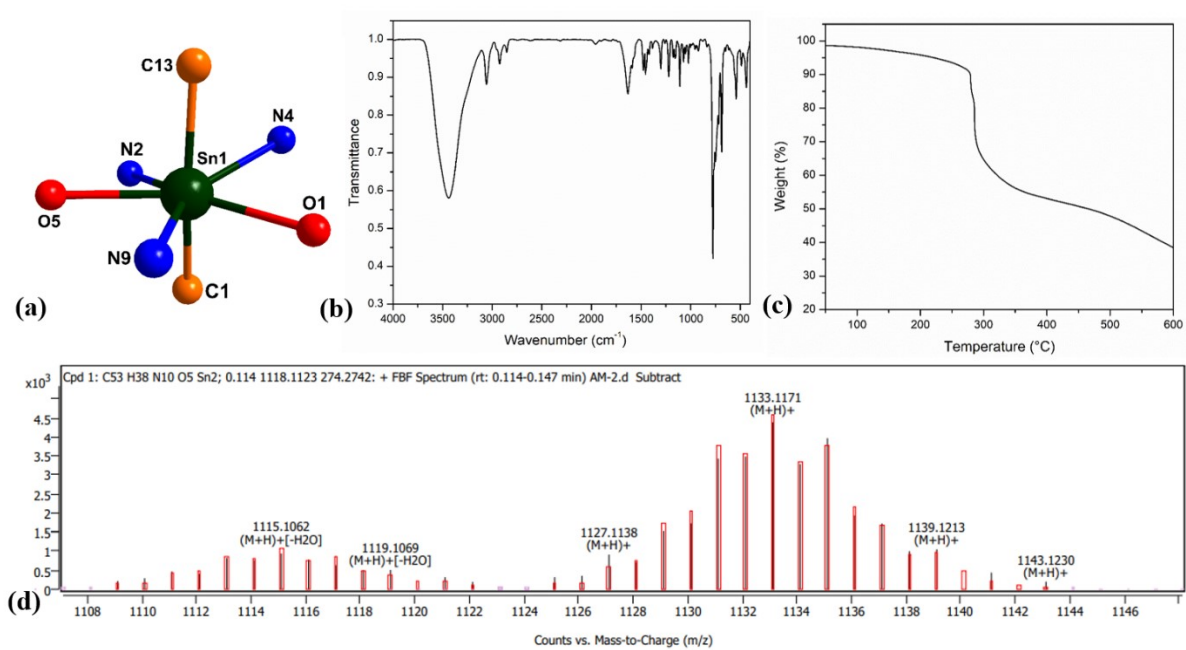


Figure S4. (a) Coordination environment of Sn center in **2**, (b) FTIR spectrum, (c) TGA plot, (d) ESI-MS spectrum complex of **2**.

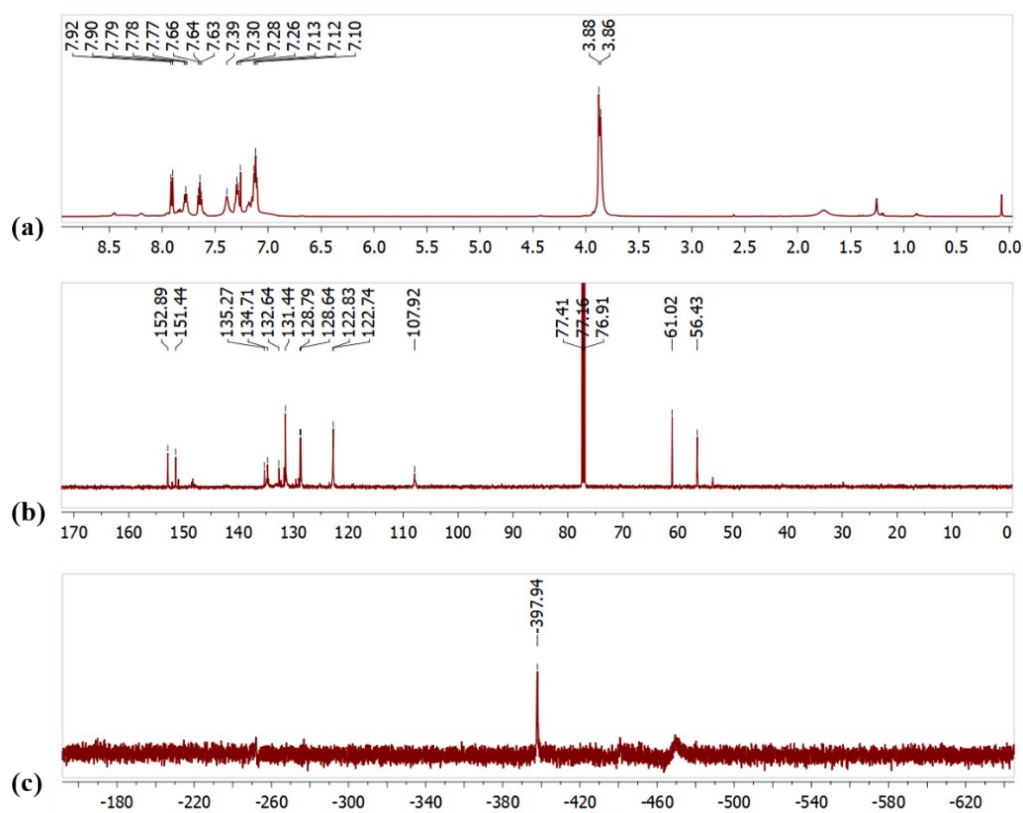


Figure S5. (a) ¹H NMR, (b) ¹³C NMR and (c) ¹¹⁹Sn NMR spectrum of complex **3** recorded in CDCl₃.

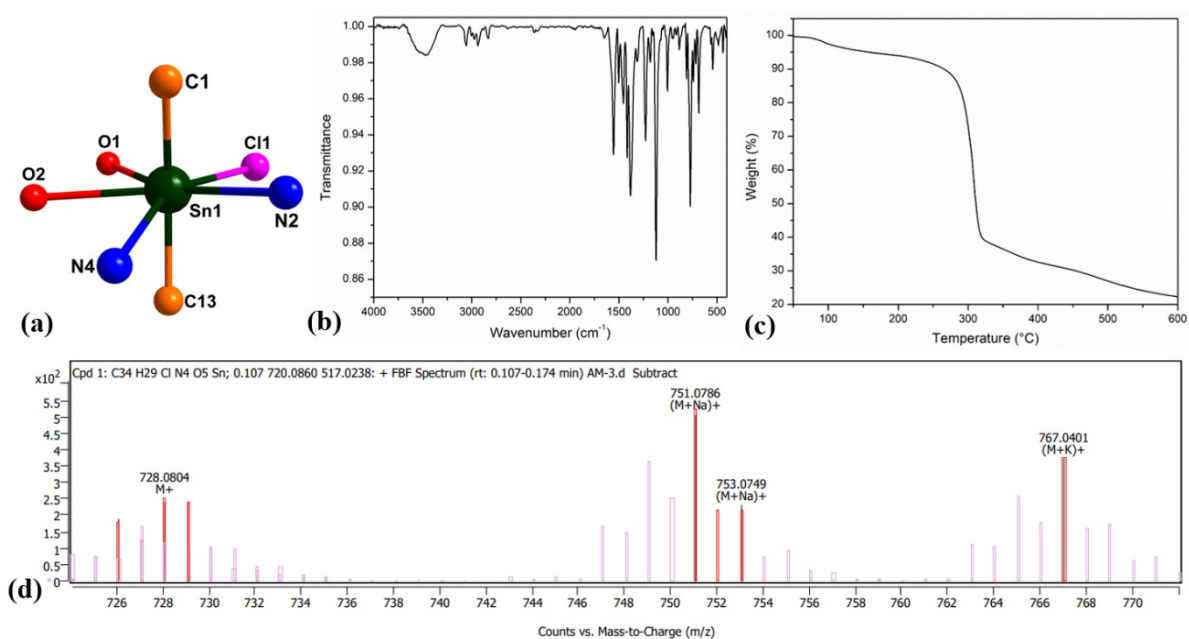


Figure S6. (a) Coordination environment of Sn center in **3**, (b) FTIR spectrum, (c) TGA plot, (d) ESI-MS spectrum complex of **3**.

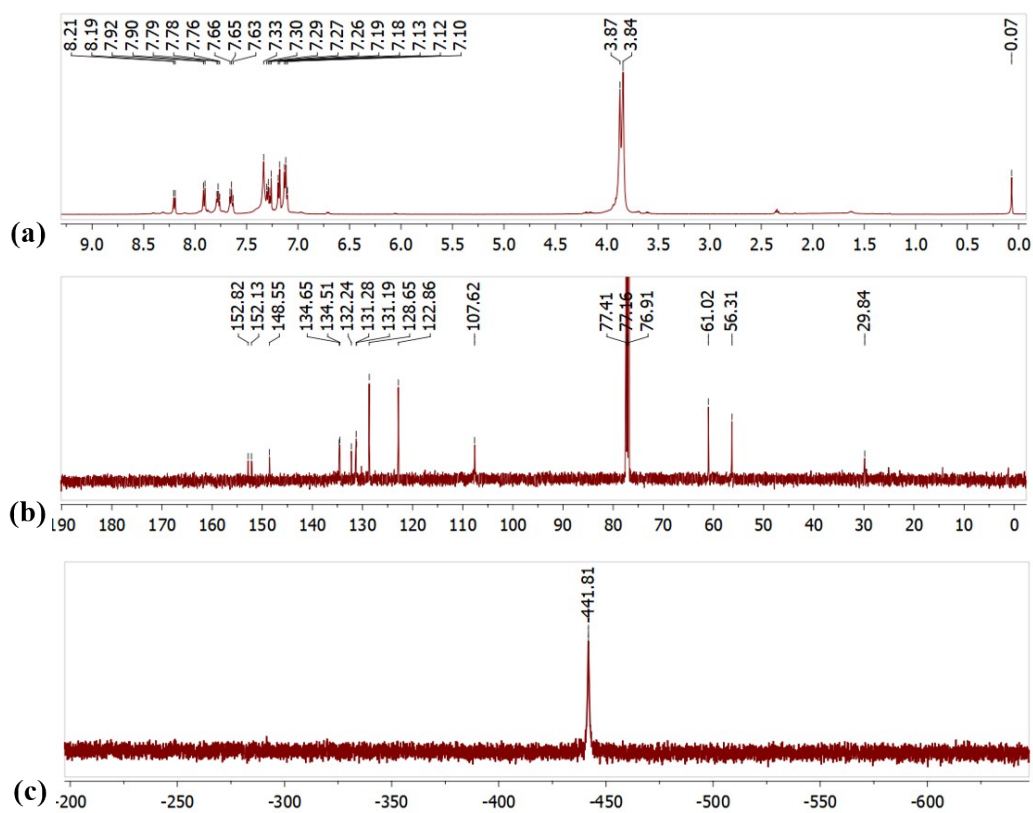


Figure S7. (a) ¹H NMR, (b) ¹³C NMR and (c) ¹¹⁹Sn NMR spectrum of complex **4** recorded in CDCl₃.

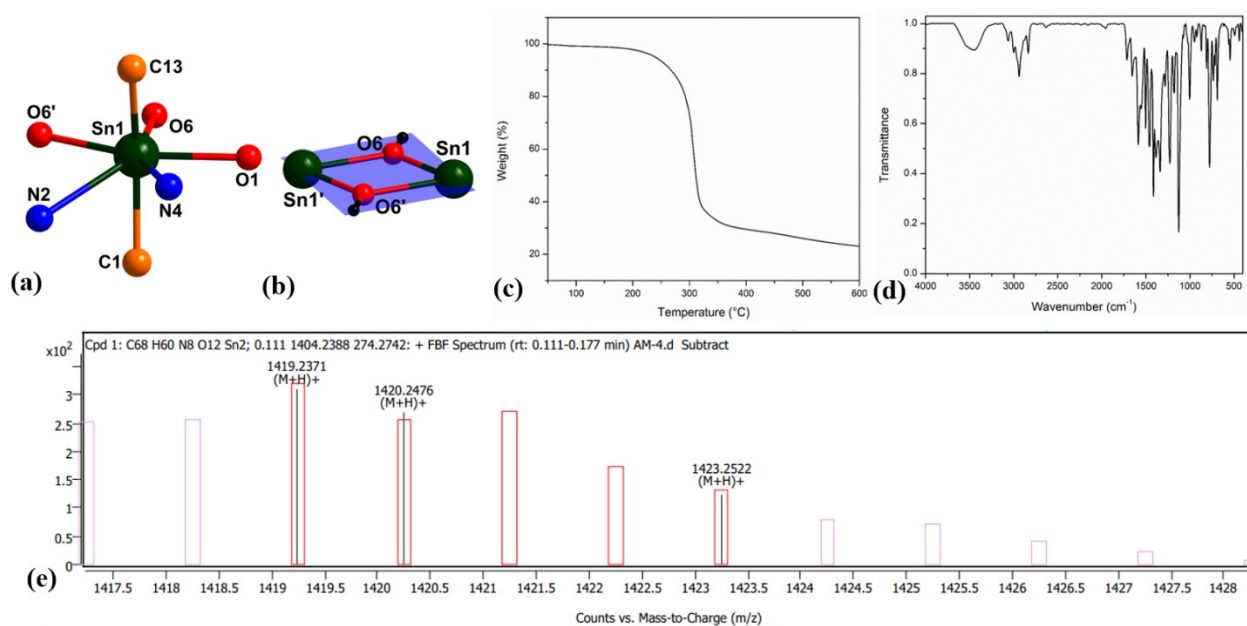


Figure S8. (a) Coordination environment of Sn center in **4**, (b) core structure of molecular plane, (c) TGA plot, (d) FTIR spectrum, (e) ESI-MS spectrum complex of **4**.

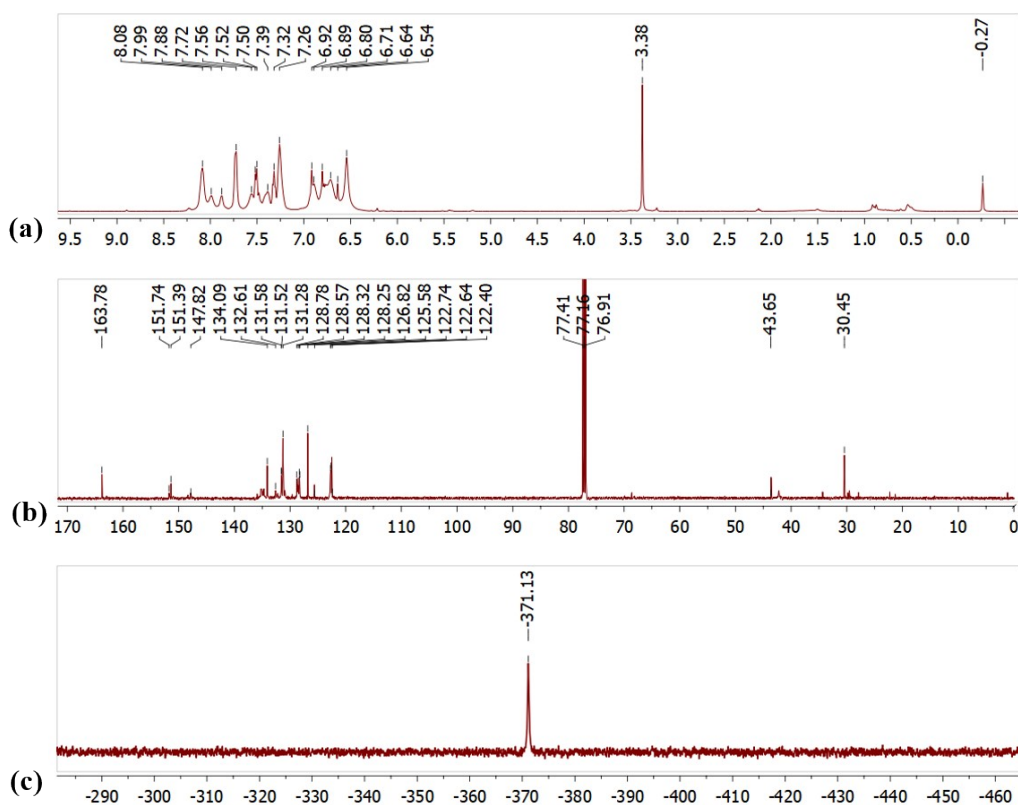


Figure S9. (a) ¹H NMR, (b) ¹³C NMR and (c) ¹¹⁹Sn NMR spectrum of complex **5** recorded in CDCl₃.

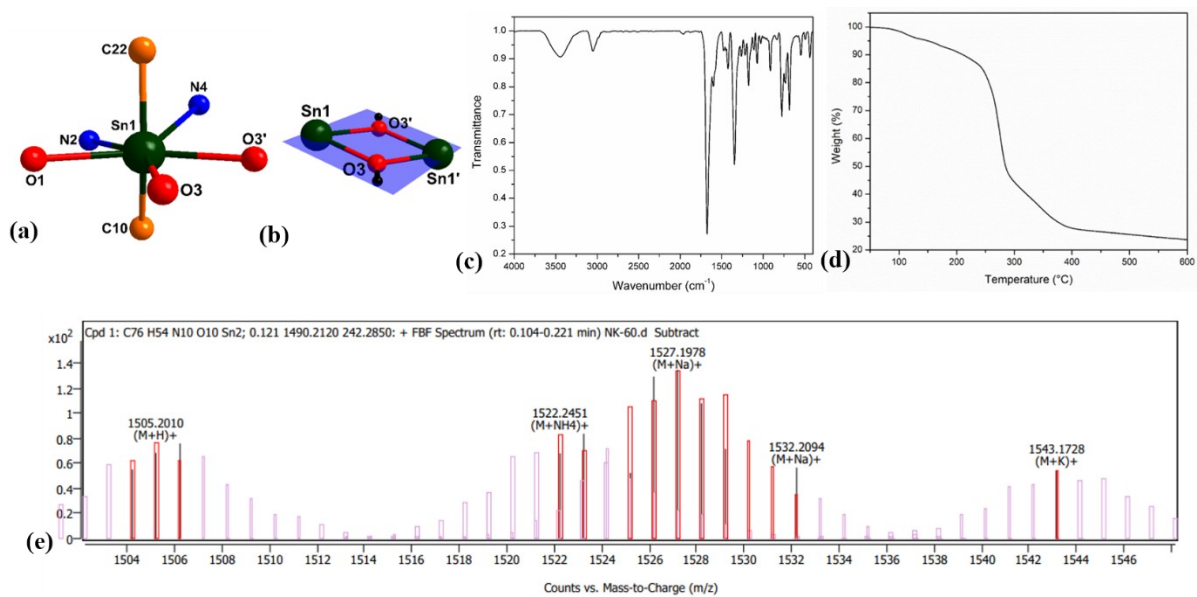


Figure S10. (a) Coordination environment of Sn center in **5**, (b) core structure of molecular plane, (c) FTIR spectrum, (d) TGA plot, (e) ESI-MS spectrum complex of **5**.

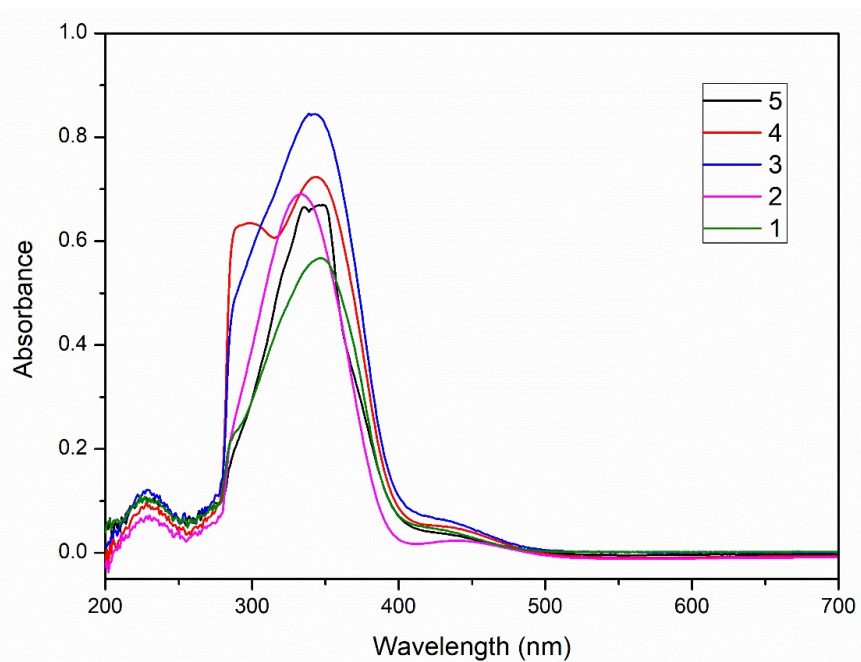


Figure S11. UV-vis spectra for complexes **1-5** (10^{-5} M conc. in CHCl_3).

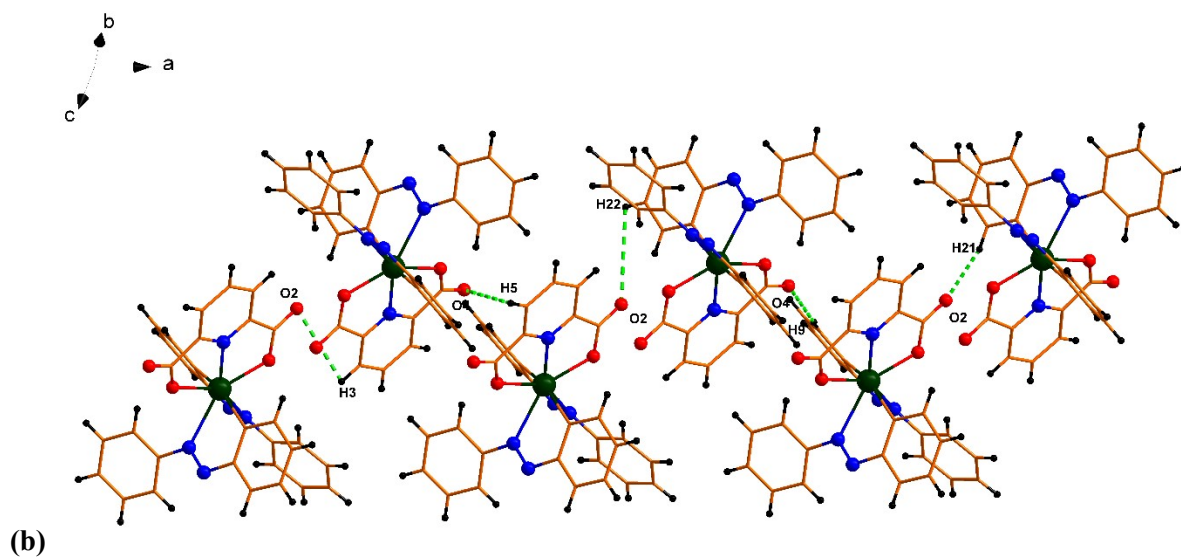
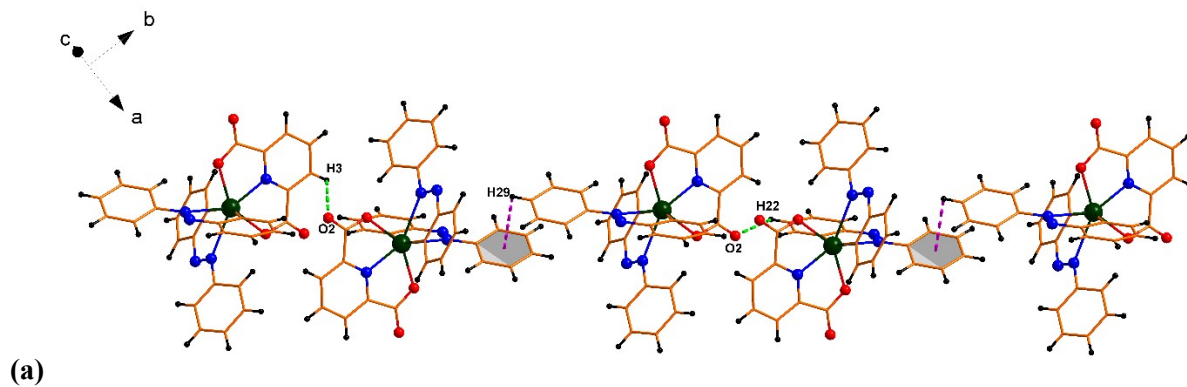
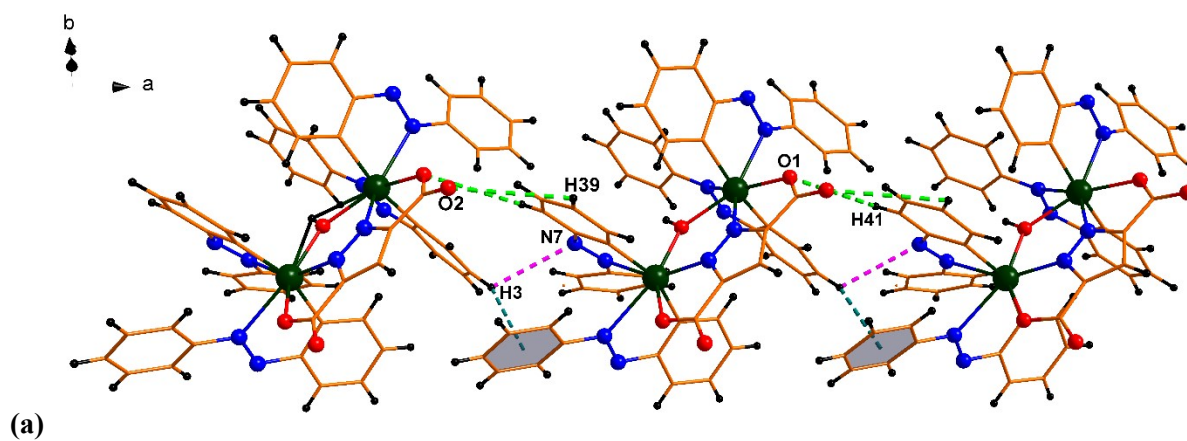
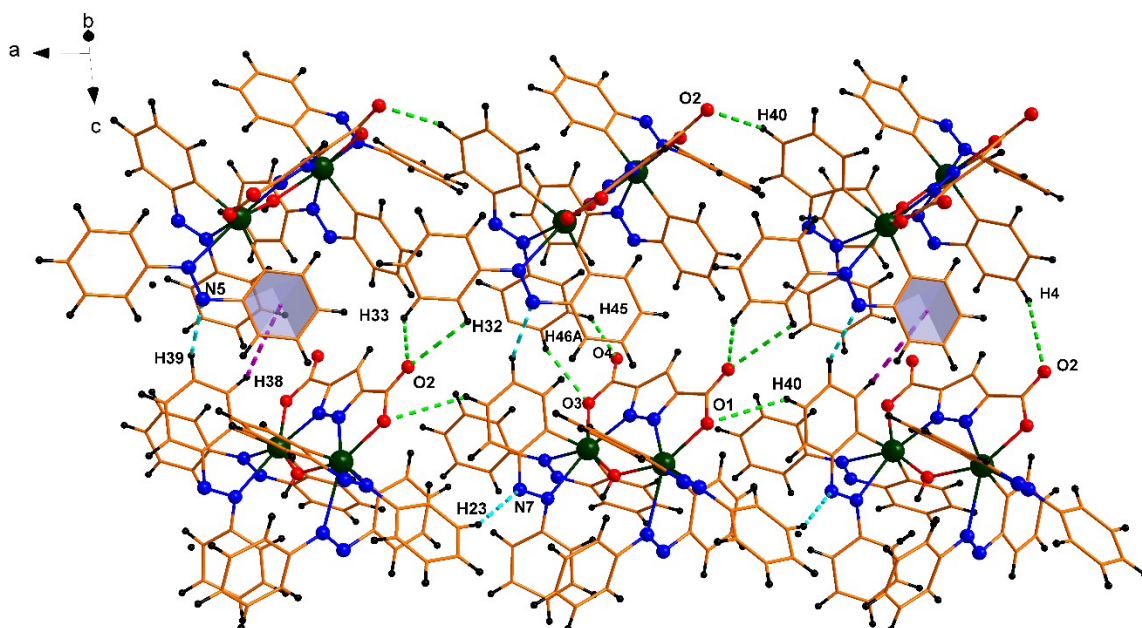


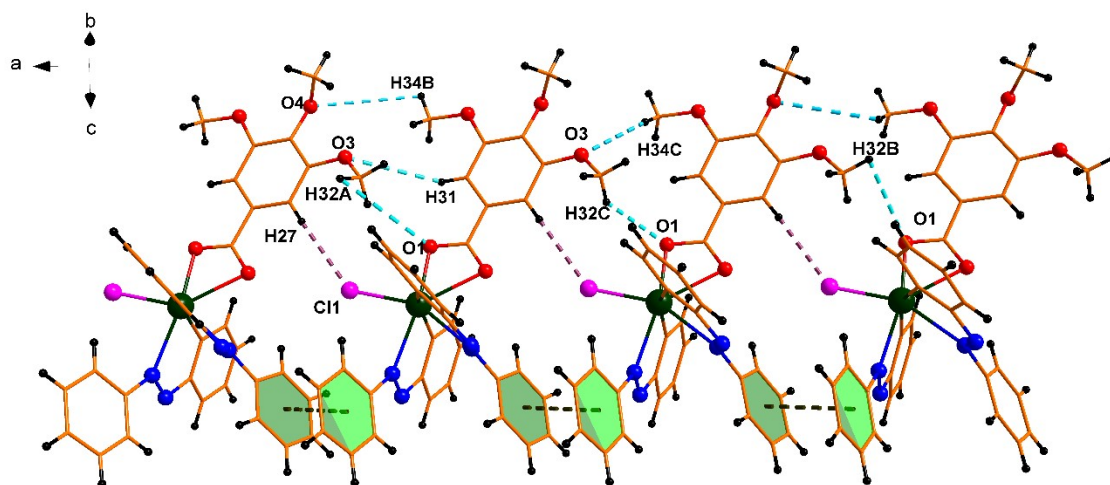
Figure S12. (a) One-dimensional supramolecular assembly formed from CH- π and CH-O interactions. Metric parameters are as follows; H29-- π , 3.604 (1) Å; H3--O2, 3.299 (2) Å; H22--O2, 3.747 (2) Å; (b) Two-dimensional supramolecular architecture assembled from CH-O interactions. Metric parameters are as follows; H21--O2, 2.348 (2) Å; H9--O4, 2.516 (2) Å; H5--O4, 3.343 (2) Å.



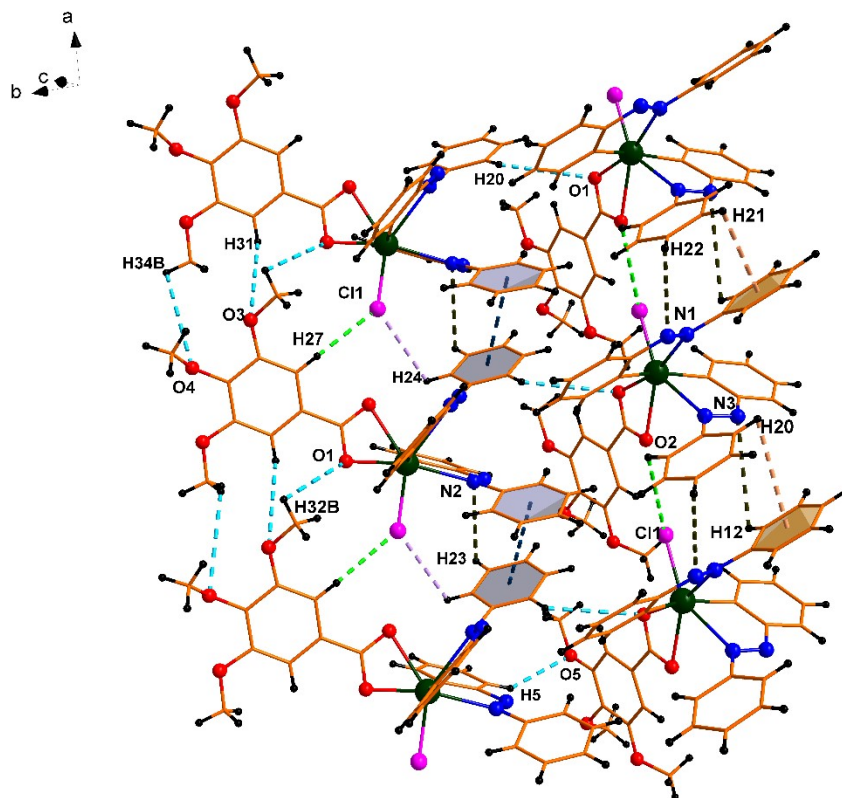


(b)

Figure S13. (a) One-dimensional supramolecular assembly formed from CH-- π , CH--N and CH--O interactions. Metric parameters are as follows; H3-- π , 2.830 (2) Å; H3--N7, 3.187 (8) Å; H39--O2, 3.903 (6) Å; H41--O1, 3.572 (6) Å; (b) Two-dimensional supramolecular architecture assembled from CH-- π , CH--N and CH--O interactions. Metric parameters are as follows; H38-- π , 3.878 (3) Å; H39--N5, 2.840 (7) Å; H23--N7, 3.277 (9) Å; H33--O2, 2.616 (7) Å; H46A--O3, 2.763 (7) Å; H4--O2, 3.403 (7) Å.



(a)



(b)

Figure S14. (a) One-dimensional supramolecular assembly formed from π - π , CH-Cl and CH-O interactions. Metric parameters are as follows; π - π , 3.807 (4) Å; H27--C11, 2.880 (2) Å; H32A--O1, 3.972 (3) Å; H31--O3, 3.444 (3) Å; H34C--O3, 2.789 (3) Å; (b) Two-dimensional supramolecular architecture assembled from π - π , CH- π , CH-Cl, CH-N and CH-O interactions. Metric parameters are as follows; π - π , 3.807 (4) Å; H21-- π , 3.531 (5) Å; H22--N1, 3.243 (4) Å; H12--N3, 3.892 (5) Å; H23--N2, 3.724 (4) Å; H24--C11, 3.342 (2) Å; H20--O1, 3.691 (3) Å.

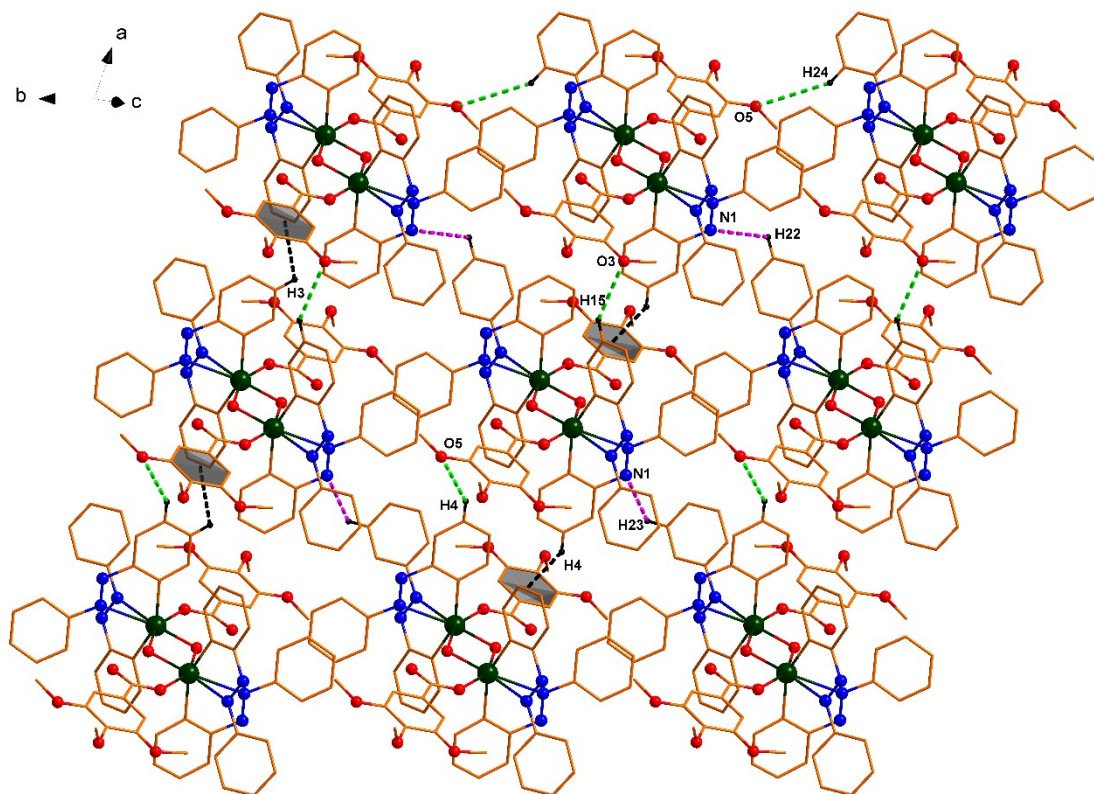
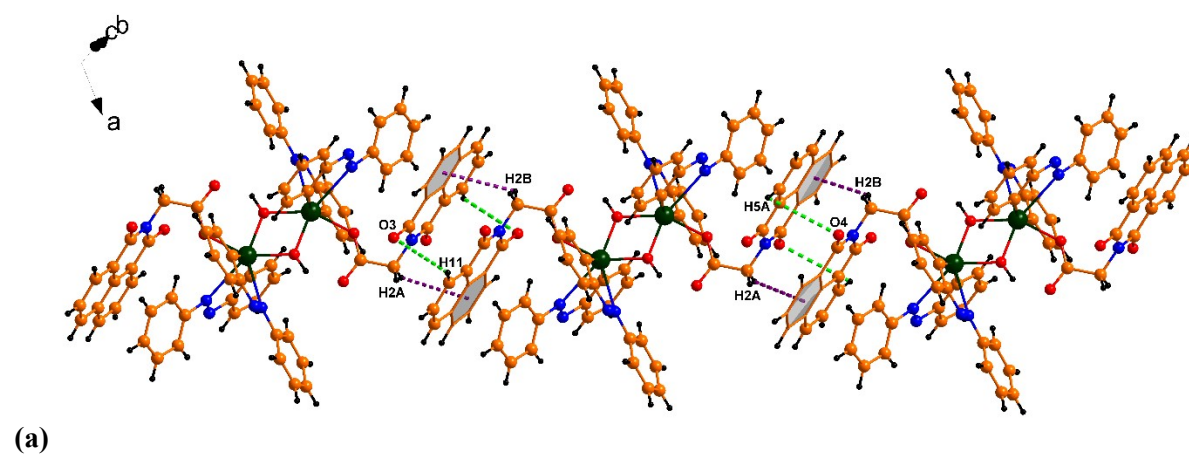
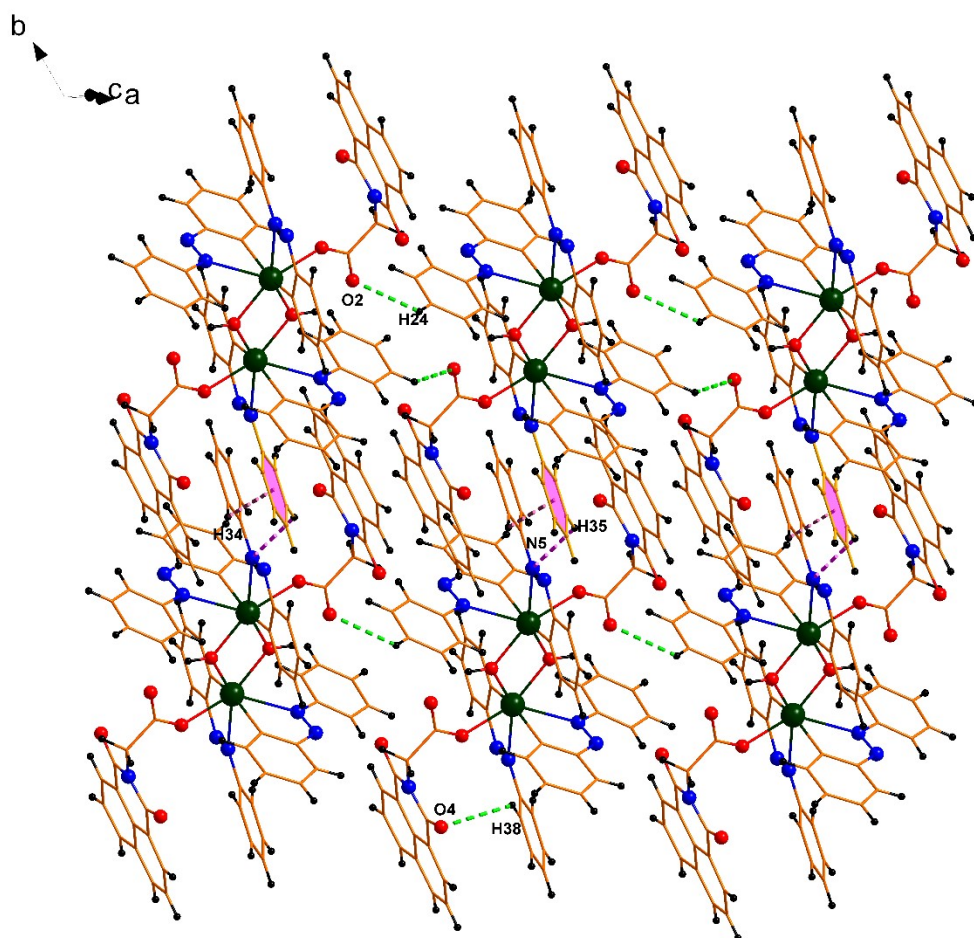


Figure S15. Two-dimensional supramolecular architecture assembled from CH- π , CH-O and CH-N interactions. H atoms are omitted for clarity. Metric parameters are as follows; H3-- π , 3.837 (5) Å; H4-- π , 2.838 (5) Å; H15--O3, 3.073 (2) Å; H24--O5, 3.569 (3) Å; H23--N1, 3.824 (2) Å; H22--N1, 3.682 (2) Å.





(b)

Figure S16. (a) One-dimensional supramolecular assembly formed from CH-- π , and CH--O interactions. Metric parameters are as follows; H2A-- π , 3.269 (3) Å; H2B-- π , 2.994 (3) Å; H11--O3, 3.597 (3) Å; H5A--O4, 3.581 (2) Å; (b) Two-dimensional supramolecular architecture assembled from CH-- π , CH--N and CH--O interactions. Metric parameters are as follows; H34-- π , 3.782 (4) Å; H38--O4, 3.068 (3) Å; H24--O2, 2.793 (3) Å; H35--N5, 3.915 (3) Å.

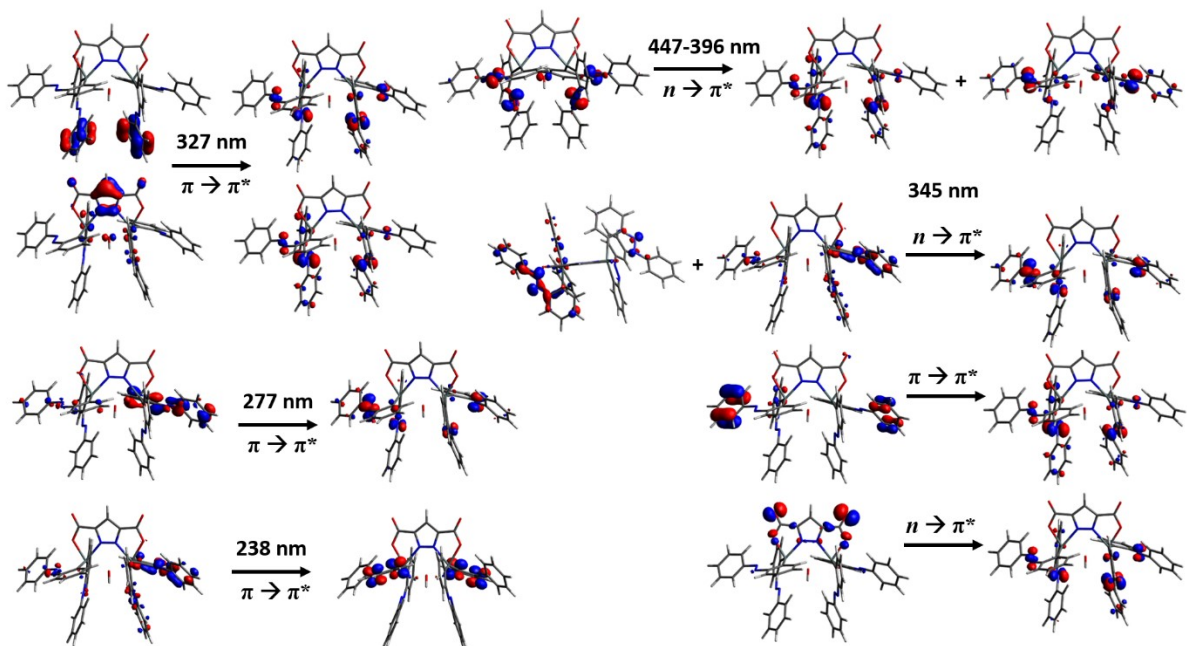


Figure S17. The molecular orbital representation of electronic transitions corresponding to the TD-DFT computed absorption spectrum of Sn complex **2**. The contour value used to plot these is 0.05 au.

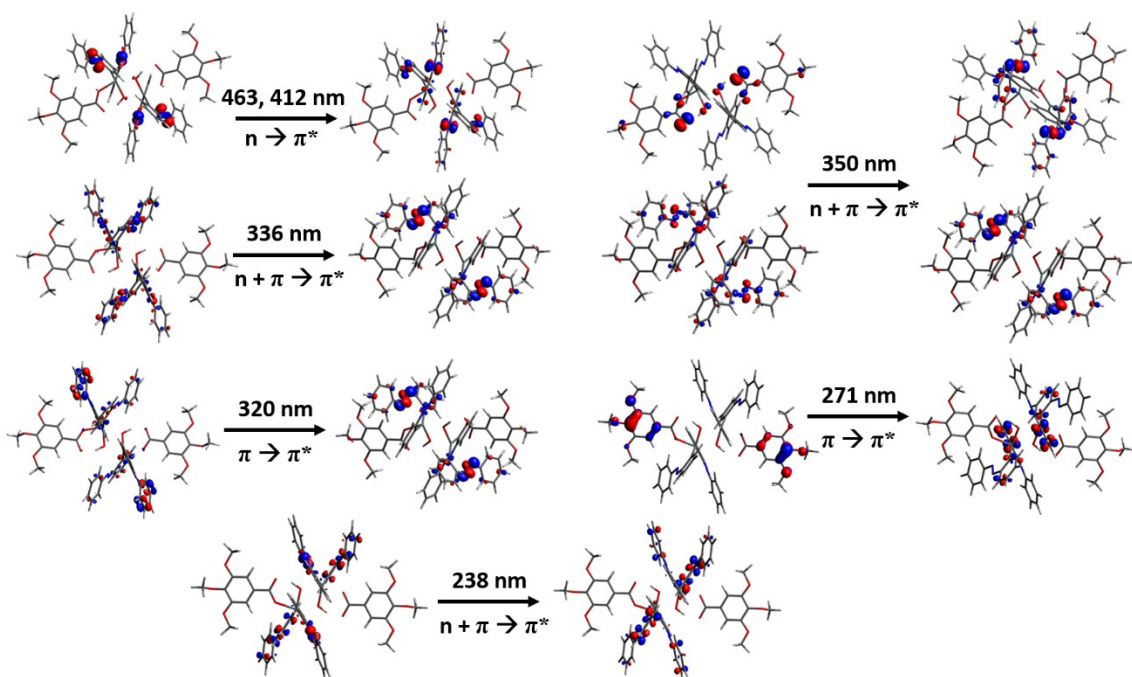


Figure S18. The molecular orbital representation of electronic transitions corresponding to the TD-DFT computed absorption spectrum of Sn complex **4**. The contour value used to plot these is 0.05 au.

References:

- (S1) G. M. Sheldrick, SHELXS-97 and SHELXL-97, Program for Crystal Structure Solution and Refinement, *University of Göttingen, Germany, 1997*.
- (S2) G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement; *University of Göttingen: Göttingen, Germany, 1997*.
- (S3) A. L. Spek, PLATON for Windows. *Utr. Univ. Netherlands 1999*.