Supporting Information

Positional isomers of (E)-2-(anthracen-9-ylmethylene)-N-(aryl)hydrazinecarbothioamide, zinc complexes and polymorphic solvates

Contents

General:

A PerkinElmer Spectrum Two FT-IR spectrometer was used to record IR spectra (4000-400 cm^{-1}) by ATR method. Powder X-ray diffraction patterns were recorded by using a Rigaku X-ray diffractometer (the source was with copper Kα, λ = 1.54 Å with 9 kW power). A Bruker Ascend-600 MHz NMR spectrometer was used for NMR spectra. Thermogravimetry and differential scanning calorimetry were recorded by using a thermal analyser (STA449 F3 Jupitor) under nitrogen with a heating rate of 10 °C min^{-1}.

Crystallographic Study: Single-crystal X-ray diffraction data were collected at 296 K with MoKα radiation (λ = 0.71073 Å) by a Bruker Nonius SMART APEX CCD diffractometer equipped with a graphite monochromator and an Apex CCD camera. Data reductions and cell refinement for Bruker Nonius SMART APEX CCD diffractometer were performed using SAINT and XPREP software. Structures were solved by direct methods and were refined by full-matrix least-squares on F^2 using SHELXL-2014 software. All non-hydrogen atoms were refined in anisotropic approximation against F^2 of all reflections. Hydrogen atoms were placed at their geometric positions by riding and refined in the isotropic approximation

Spectroscopic details of the ligands and complexes:

3-OCH$_3$HATU·DMF: Yield = 79 %. IR (Neat, cm^{-1}): 3284 (w), 2928 (w), 1627 (s), 1603 (s), 1538 (s), 1494 (s), 1414 (m), 1396 (s), 1300 (m), 1268 (m), 1232 (s), 1173 (s), 1156 (s), 1072 (s), 1038 (m), 1017 (m), 981 (m), 955 (s), 898 (s), 843 (s), 825 (s). ^{1}HNMR (600 MHz, DMSO-d$_6$, ppm): 12.08 {s, N-H (1)}, 9.96 {s, N-H (2)}, 9.41 (s, 1H), 8.73 (s, 1H), 8.58 (d, J = 9 Hz, 2H), 8.16 (d, J = 8.4 Hz, 2H), 7.66 (t, J = 9 Hz, 2H), 7.59 (t, J = 7.2 Hz, 2H), 7.35 (s, 1H), 7.26-7.2 (m, 2H), 6.75 (d, J = 8.4 Hz, 1H), 3.1 (s, 3H), 2.93 (s, 3H), 2.78 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d$_6$): 175.71, 169.60, 159.02, 142.55, 140.14, 130.89, 129.71, 129.53, 128.98, 128.81, 127.34, 125.65, 125.13, 124.83, 117.06, 110.58, 110.55, 55.12, 37.45, 34.50, 21.43.

4-OCH$_3$HATU: Yield = 86 %. IR (Neat, cm^{-1}): 3333 (m), 3138 (m), 2985 (w), 1740 (m), 1538 (s), 1512 (s), 1416 (m), 1353 (s), 1298 (s), 1271 (s), 1271 (s), 1240 (s), 1215 (s),1172 (m), 1060 (s), 1030 (s), 949 (s), 893 (s), 838 (s), 807 (s). ^{1}HNMR (600 MHz, DMSO-d$_6$, ppm): 11.98 {s, N-H (1)}, 9.90 {s, N-H (2)}, 9.39 (s, 1H), 8.73 (s, 1H), 8.59 (d, J = 9 Hz, 2H), 8.16 (d, J = 8.4 Hz, 2H), 7.65 (t, J = 9 Hz, 2H), 7.59 (t, J = 7.8 Hz, 2H), 7.44 (d, J = 9 Hz, 2H), 6.91 (d, J = 9 Hz, 2H), 3.75 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d$_6$): 176.36, 156.86, 142.33, 134.61, 131.96, 130.90, 129.70, 129.44, 128.96, 127.32, 127.09, 126.80, 125.65, 125.24, 124.90, 113.28, 55.25.

23-ClHATU: Yield = 83 %. IR (Neat, cm^{-1}): 3305 (m), 3140 (m), 2984 (w), 1548 (s), 1505 (s), 1454 (s), 1413 (s), 1395 (s), 1331 (s), 1297 (s), 1238 (s), 1179 (s), 1159 (m), 1072 (s), 1046 (s), 1017 (s), 961 (m), 943 (s), 920 (m), 882 (s), 838 (s), 804 (s). ^{1}HNMR (600 MHz, DMSO-d$_6$, ppm): 12.32 {s, N-H (1)}, 10.09 {s, N-H (2)}, 9.46 (s, 1H), 8.76 (s, 1H), 8.65 (d, J = 9.6 Hz, 2H), 8.17 (d, J = 8.4 Hz, 2H), 7.94 (d, J = 9.6 Hz, 1H), 7.66 (t, J = 7.8 Hz, 2H), 7.6 (t, J = 7.8 Hz, 2H), 7.55 (d, J = 7.8 Hz, 1H), 7.41 (t, J = 8.4 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d$_6$): 176.19, 143.17, 138.33, 131.54, 130.91, 129.94, 129.75, 129.06, 128.18, 127.80, 127.57, 127.57, 127.48, 125.70, 124.79, 124.63.

34-ClHATU: Yield = 92 %. IR (Neat, cm^{-1}): 3315 (m), 3188 (w), 1620 (m), 1592 (s), 1577 (m), 1535 (s), 1506 (m), 1474 (s), 1422 (s), 1382 (s), 1358 (s), 1252 (s), 1189 (s), 1134 (s), 1077 (s), 1021 (s), 960 (m), 941 (m), 889 (s), 842 (s), 809 (s). ^{1}HNMR (600 MHz, DMSO-d_6, ppm): 12.22 {s, N-H (1)}, 10.21 {s, N-H (2)}, 9.41 (s, 1H), 8.74 (s, 1H), 8.56 (d, J = 9 Hz, 2H), 8.16 (d, J = 7.8 Hz, 2H), 8.0 (s, 1H), 7.66-7.64 (m, 3H), 7.6-7.58 (m, ^{13}C NMR (125 MHz, DMSO-d_6): 175.96, 143.29, 139.30, 130.84, 130.05, 129.73, 129.71, 129.57, 128.93, 127.34, 126.87, 126.59, 125.64, 125.39, 125.06, 124.84.

[Zn{3-OCH$_3$ATU)}$_2$·DMF]: Yield = 66 % (based on Zn). IR (Neat, cm^{-1}): 3265 (w), 2927 (w), 1655 (s), 1604 (s), 1546 (s), 1476 (s), 1444 (s), 1405 (s), 1359 (s), 1330 (s), 1307 (m), 1224 (s), 1187 (m), 1170 (s), 1156 (s), 1090 (s), 1072 (s), 1041 (s), 957 (m), 940 (s), 892 (s), 852 (s), 843 (s). ^{1}HNMR (600 MHz, DMSO-d_6, ppm): 9.26 {s, N-H (2), 2H}, 8.74 (s, 2H), 8.64 (s, 2H), 8.20 (d, J = 10.2 Hz, 4H), 7.95 (d, J = 10.2 Hz, 4H), 7.95 (s, 2H), 7.60-7.56 (m, 8H), 6.71 (s, 2H), 6.43 (d, J = 6 Hz, 2H), 6.33 (t, J = 8.4 Hz, 2H), 6.11 (d, J = 8.4 Hz, 2H), 2.95 (s, 6H), 2.88 (s, 6H), 2.73 (s, 6H). ^{13}CNMR (125 MHz, DMSO-d_6): 171.31, 162.37, 158.80, 148.88, 141.63, 130.86, 129.47, 128.85, 128.13, 127.98, 127.85, 126.55, 125.65, 125.44, 112.08, 107.07, 104.58, 54.10, 35.82, 30.81.

[Zn{4-OCH$_3$ATU)}$_2$·3DMF]: Yield = 69 % (based on Zn). IR (Neat, cm^{-1}): 3254 (w), 2925 (w), 1740 (m), 1660 (s), 1506 (s), 1471 (s), 1405 (s), 1384 (m), 1298 (s), 1232 (s), 1175 (s), 1080 (s), 1030 (s), 939 (m), 891 (s), 827 (s). ^{1}HNMR (600 MHz, DMSO-d_6, ppm): 9.21 {s, N-H (2), 2H}, 8.76 (s, 2H), 8.66 (s, 2H), 8.22 (d, J = 9 Hz, 4H), 7.97 (d, J = 6 Hz, 4H), 7.95 (s, 3H), 7.59 (t, J = 4.8 Hz, 8H), 6.75 (d, J = 9 Hz, 4H), 6.03 (d, J = 9 Hz, 4H), 3.5 (s, 6H), 2.87 (s, 9H), 2.72 (s, 9H). ^{13}C NMR (125 MHz, DMSO-d_6): 176.52, 162.38, 153.46, 147.77, 133.93, 130.82, 129.64, 128.83, 128.04, 127.87, 126.48, 125.66, 120.94, 112.47, 54.86, 35.84, 30.82.

[Zn{23-ClATU)}$_2$·CHCl$_3$]-2: Yield = 61 % (based on Zn). IR (Neat, cm^{-1}): 3403 (m), 3050 (w), 1583 (s), 1521 (s), 1477 (s), 1450 (s), 1395 (s), 1357 (s), 1305 (s), 1205 (s), 1181 (s), 1079 (s), 1049 (s), 1016 (m), 941 (s), 889 (s), 835 (s), 825 (s). ^{1}HNMR (600 MHz, DMSO-d_6, ppm): 8.78 {s, N-H (2), 2H}, 8.73 (s, 2H), 8.32 (s, 2H), 8.21 (s, 2H), 8.19 (d, 4H), 7.9 (d, J = 8.4 Hz, 4H), 7.58-7.63 (m, 8H), 6.93 (d, J = 8.4 Hz, 2H), 6.76 (d, J = 8.4 Hz, 2H), 6.07 (t, J= 8.4 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): 171.75, 150.65, 137.60, 130.95, 130.66, 128.97, 128.83, 128.12, 127.95, 126.63, 126.19, 125.66, 125.47, 123.87, 123.08, 120.03, 79.20.

[Zn{34-ClATU)}$_2$·CHCl$_3$] : Yield = 59 % (based on Zn). IR (Neat, cm^{-1}): 3320 (m), 1580 (s), 1530 (s), 1469 (s), 1384 (s), 1364 (s), 1302 (s), 1240 (s), 1191 (s), 1158 (s), 1134 (s), 1073 (s), 1046 (s), 1026 (s), 940 (s), 919 (s), 880 (s), 836 (s), 820 (s), 803 (s). ^{1}HNMR (600 MHz, DMSO-

d_6, ppm): 9.63 {s, N-H (2), 2H}, 8.79 (s, 2H), 8.73 (s, 2H), 8.32 (s, 2H), 8.23 (d, J = 9.6 Hz, 4H), 7.91 (d, J = 9.6 Hz, 4H), 7.60-7.58 (m, 8H), 7.24 (s, 2H), 6.84 (d, J = 9 Hz, 2H), 6.72 (d, J= 8.4 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): 171.18, 150.39, 140.36, 130.91, 130.10, 129.07, 128.98, 128.43, 127.71, 126.68, 125.65, 125.22, 122.05, 120.39, 119.05, 79.20.

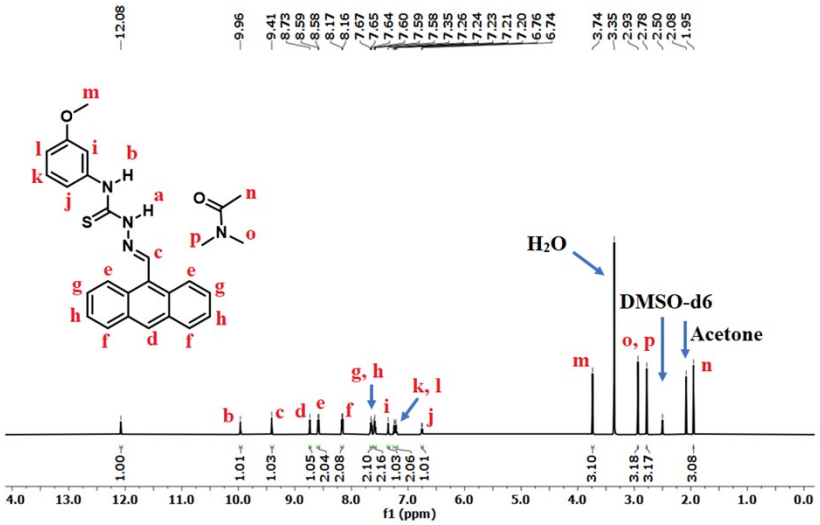


Figure S1: ^{1}HNMR (DMSO-d_6, 600 MHz) spectra of the 3-OCH$_3$HATU·DMF

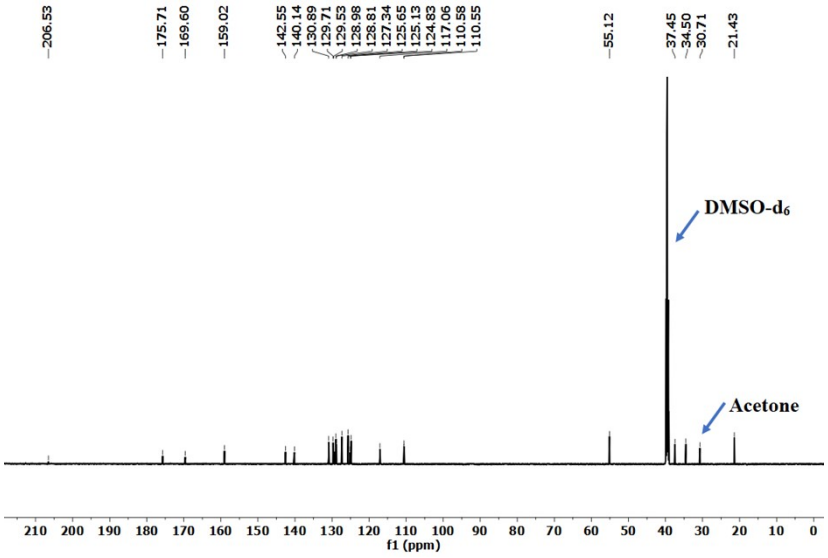


Figure S2: ^{13}CNMR (125 MHz, DMSO-d_6) spectra of the 3-OCH$_3$HATU·DMF

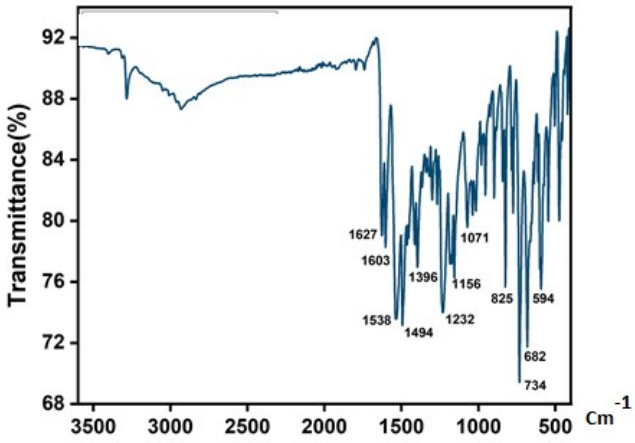


Figure S3: FT-IR spectrum (neat) of the 3-OCH_3HATU·DMF

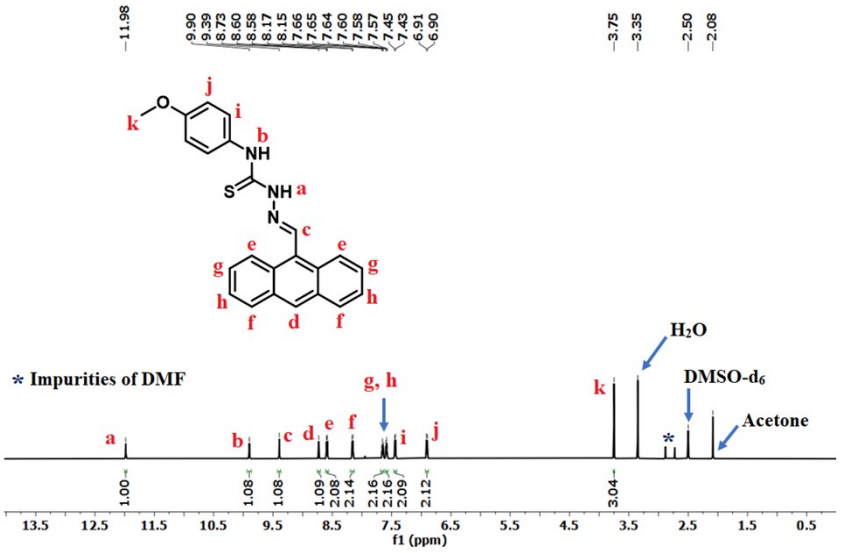


Figure S4: ^{1}HNMR (DMSO-d_6/ acetone-d_6, 600 MHz) spectra of the 4-OCH_3HATU

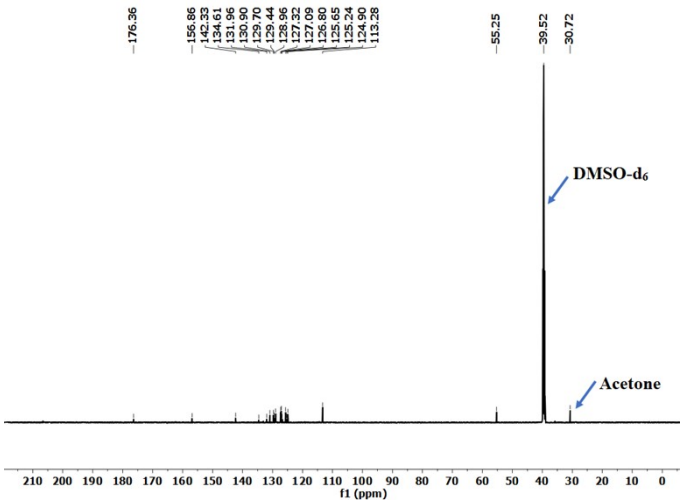


Figure S5: ^{13}CNMR (125 MHz, DMSO-$d_{6/}$ acetone-d_6) spectra of the 4-OCH_3HATU

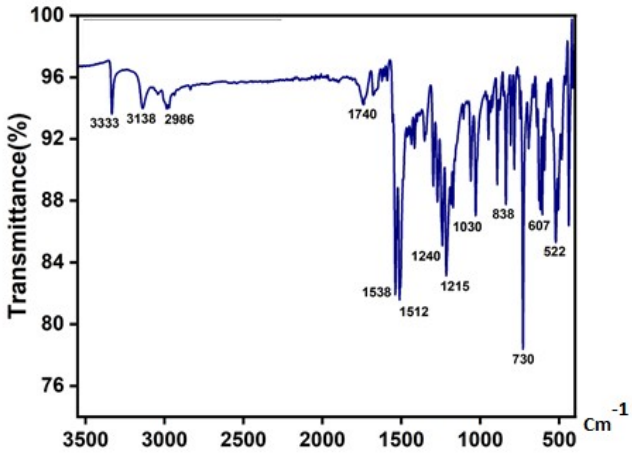


Figure S6: FT-IR spectrum (neat) of the 4-OCH_3HATU

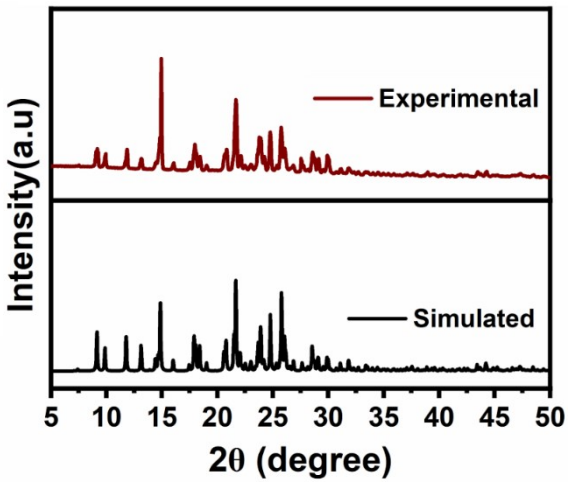


Figure S7: Powder X-ray diffraction patterns of the 4-OCH_3HATU

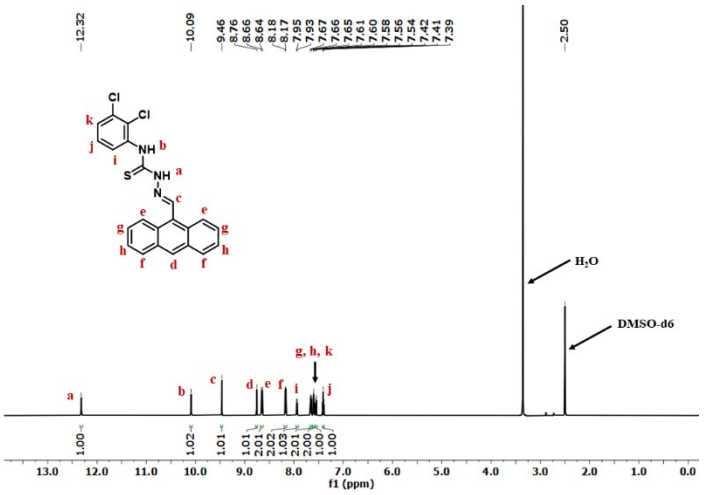


Figure S8: ^{1}H-NMR (DMSO-d_6, 600 MHz) spectra of the 23-ClHATU

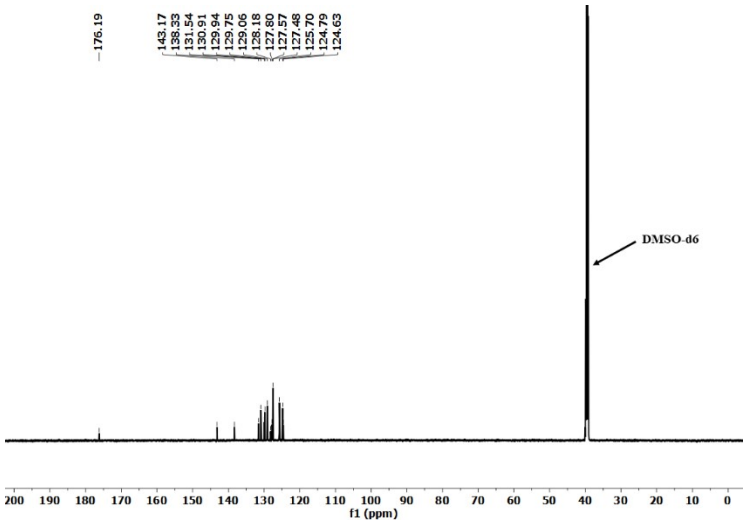


Figure S9: ^{13}CNMR (125 MHz, DMSO-d_6) spectra of the 23-ClHATU

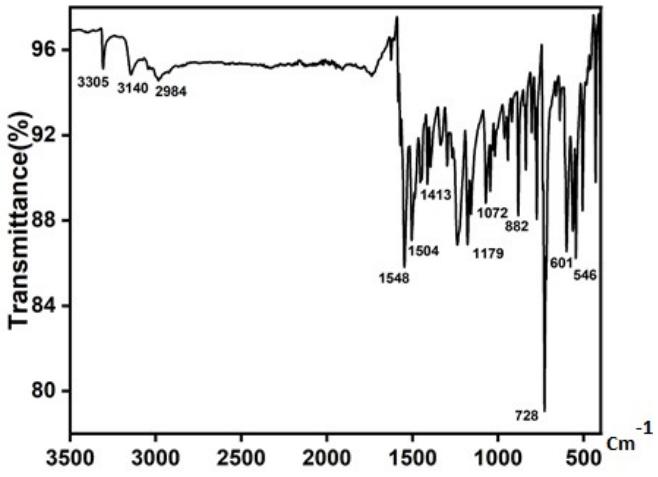


Figure S10: FT-IR spectrum (neat) of the 23-ClHATU

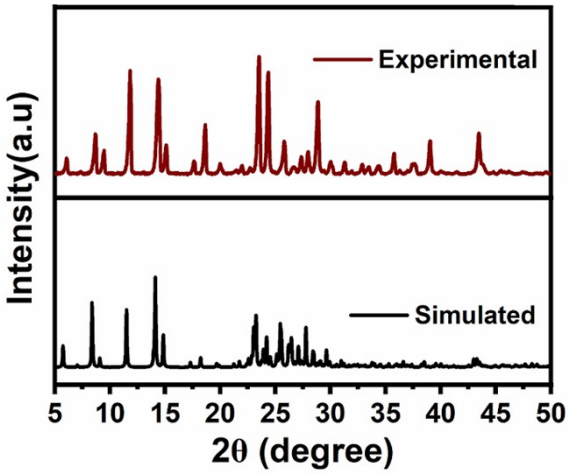


Figure S11: Powder X-ray diffraction patterns of the 23-ClHATU

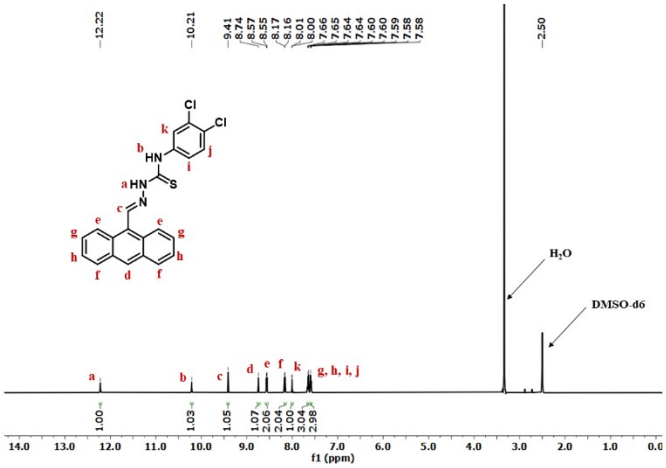


Figure S12: ^{1}HNMR (DMSO-d_6, 600 MHz) spectra of the 34-ClHATU

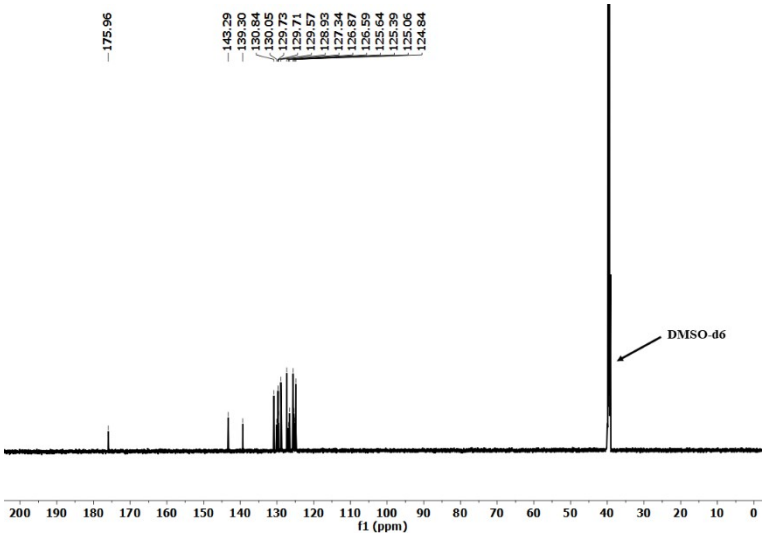


Figure S13: ^{13}CNMR (125 MHz, DMSO-d_6) spectra of the 34-ClHATU

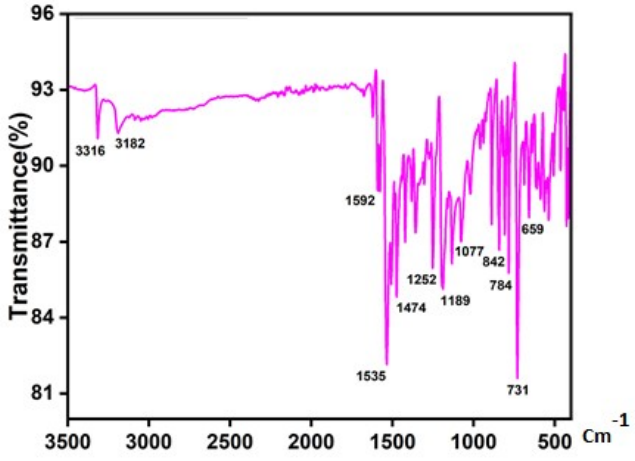


Figure S14: FT-IR spectrum (neat) of the 34-ClHATU

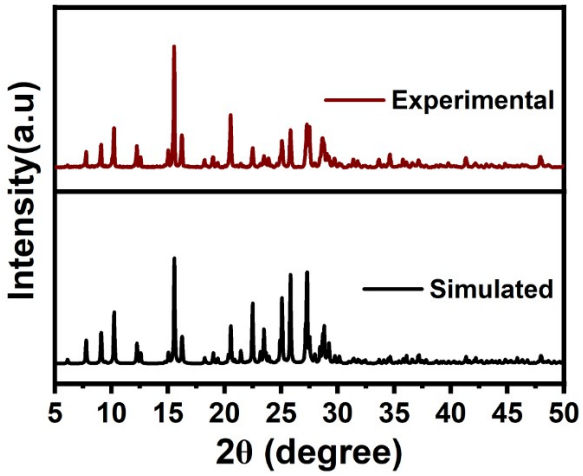


Figure S15: Powder X-ray diffraction patterns of the 34-ClHATU

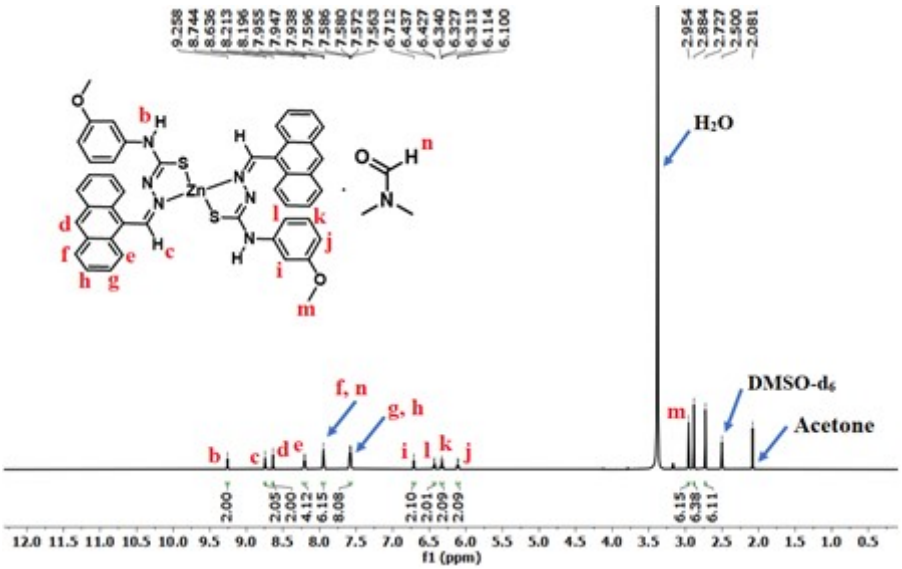


Figure S16: ^{1}HNMR (DMSO-$d_{6/}$ acetone-d_6, 600 MHz) spectra of the [Zn{3-OCH_3ATU)}$_2$·DMF]

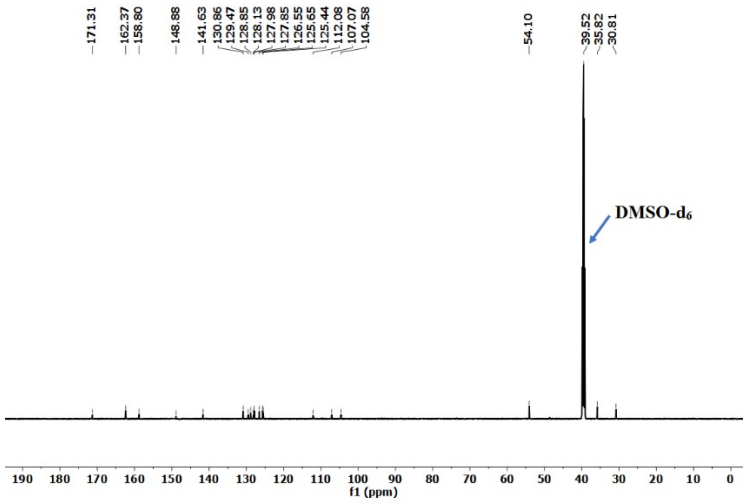


Figure S17: ^{13}CNMR (125 MHz, DMSO-d_6) spectra of the [Zn{3-OCH_3ATU)}$_2$·DMF]

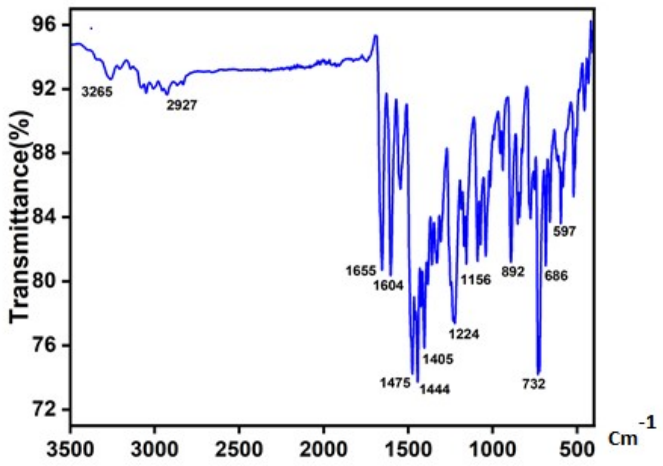


Figure S18: FT-IR spectrum (neat) of the [Zn{3-OCH_3ATU)}$_2$·DMF]

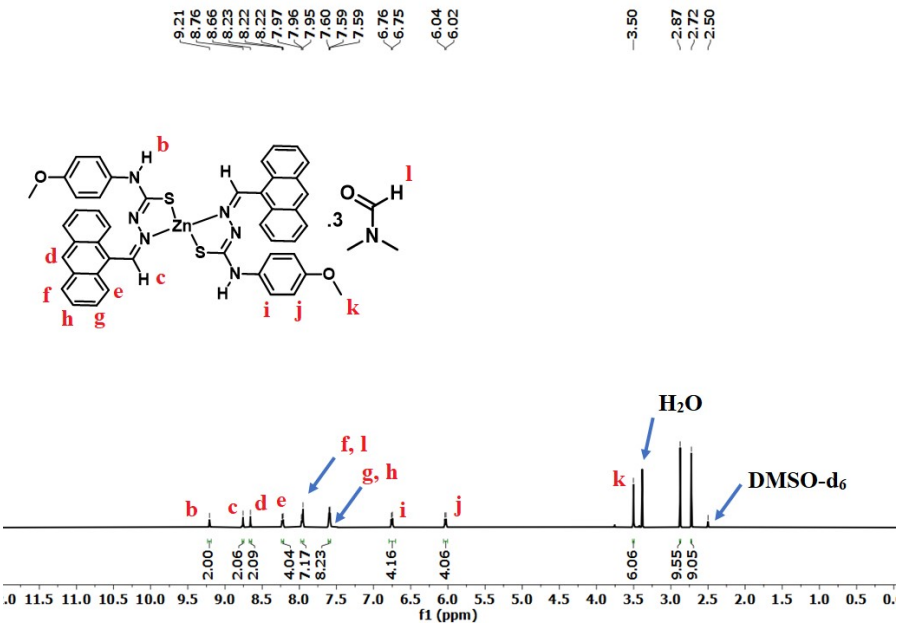


Figure **S19**: ^{1}HNMR (DMSO-d_6, 600 MHz) spectra of the [Zn{4-OCH_3ATU)}$_2$·3DMF]

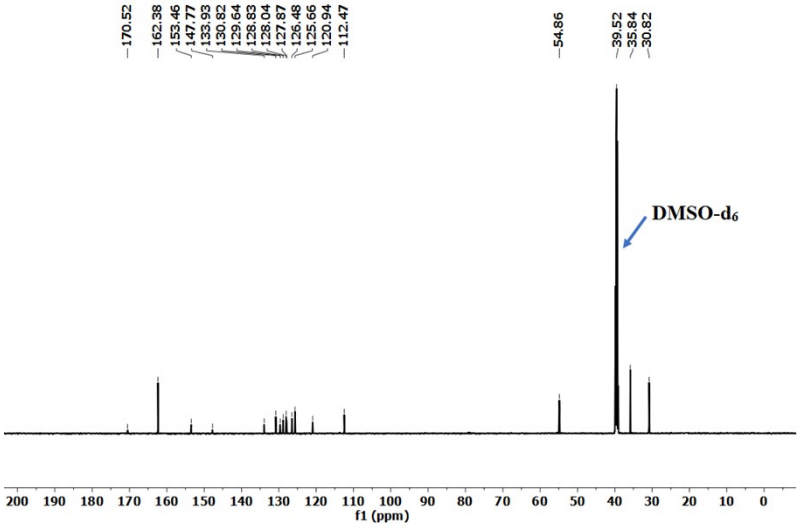


Figure S20: ^{13}CNMR (125 MHz, DMSO-d_6/ acetone-d_6) spectra of the [Zn{4-OCH_3ATU)}$_2$·3DMF]

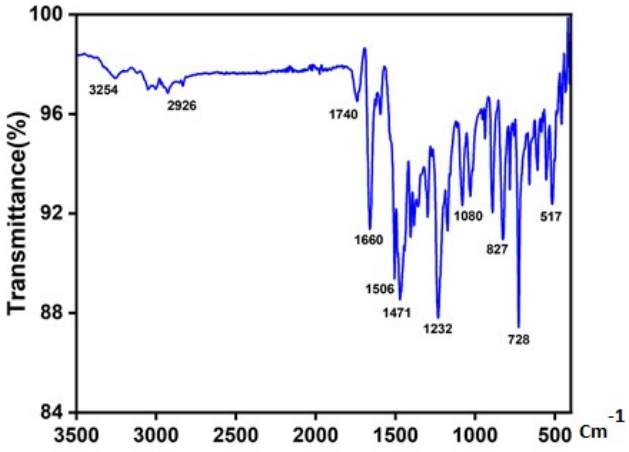


Figure S21: FT-IR spectrum (neat) of the [Zn{4-OCH_3ATU)}$_2$·3DMF]

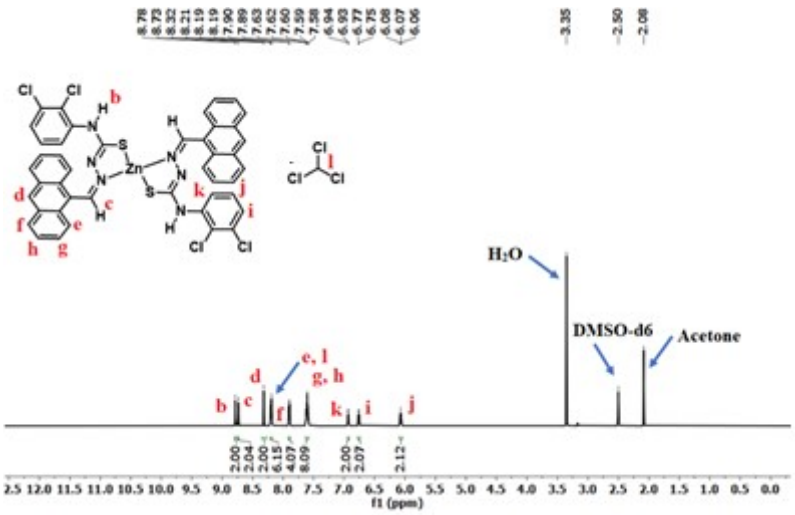


Figure **S**22: ^{1}HNMR (DMSO-d_6 acetone-d_6, 600 MHz) spectra of the [Zn{23-ClATU)}$_2$·$CHCl_3$]-1

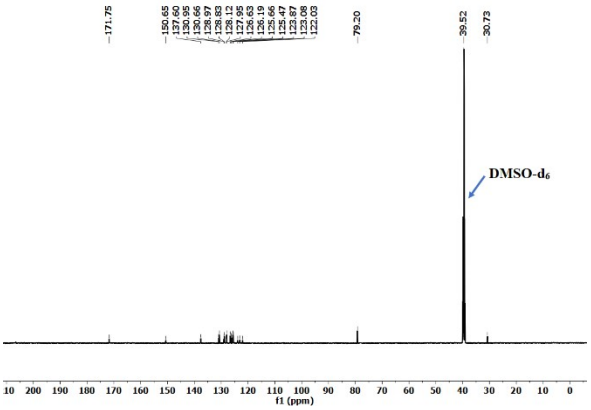


Figure **S**23: ^{13}CNMR (125 MHz, DMSO-d_6 /acetone-d_6) spectra of the [Zn{23-ClATU)}$_2$·$CHCl_3$]-1

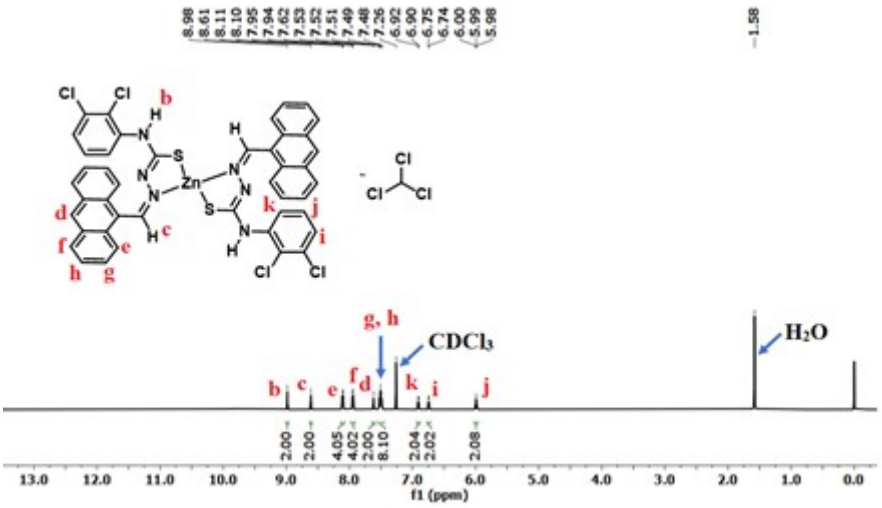


Figure S24: ^{1}HNMR ($CDCl_3$, 600 MHz) spectra of the [Zn{23-ClATU)}$_2$·$CHCl_3$]-2

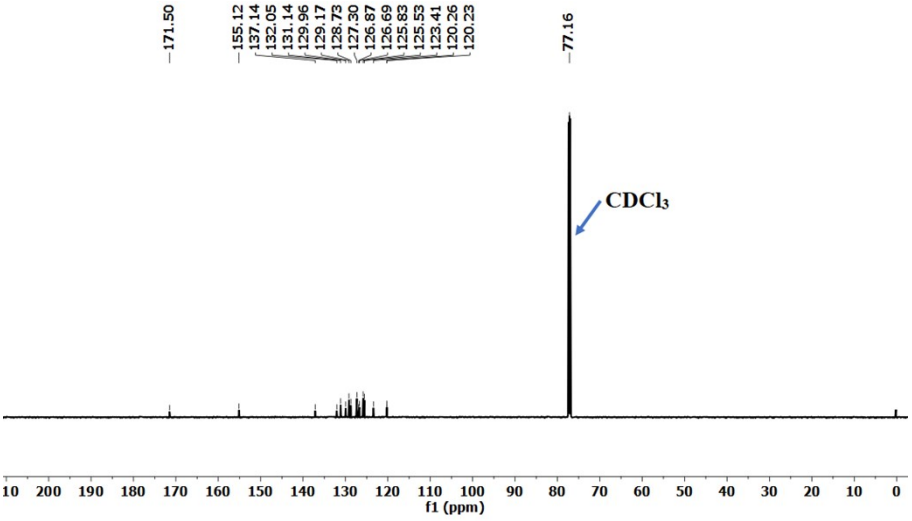


Figure S25: ^{13}CNMR (125 MHz, $CDCl_3$) spectra of the [Zn{23-ClATU)}$_2$·$CHCl_3$]-2

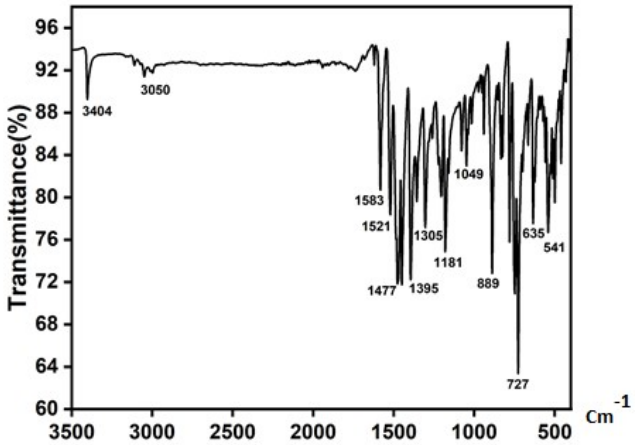


Figure S26: FT-IR spectrum (neat) of the [Zn{23-ClATU)}$_2$·CHCl$_3$]-2

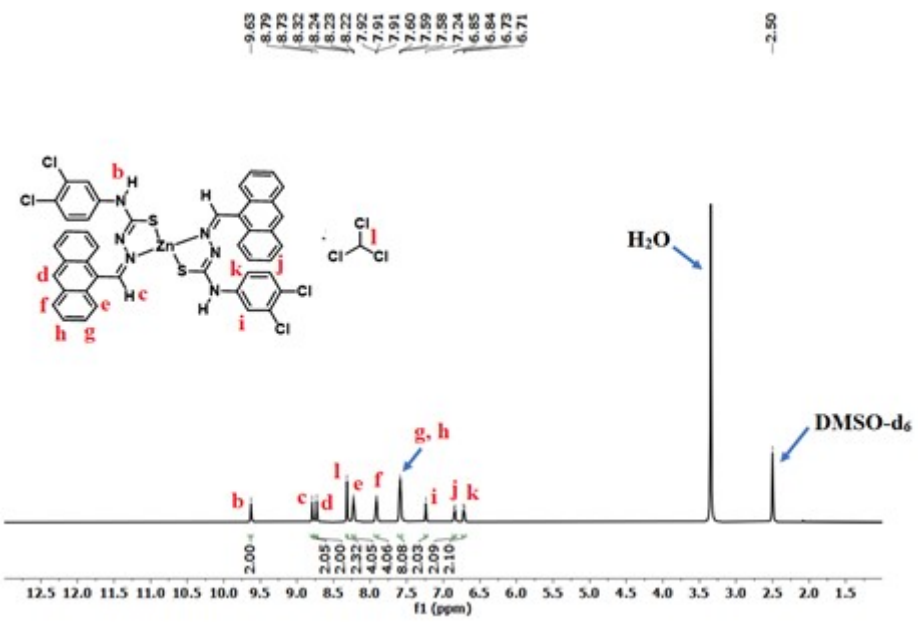


Figure S27: ^{1}HNMR (DMSO-d$_6$, 600 MHz) spectra of the [Zn{34-ClATU)}$_2$·CHCl$_3$]

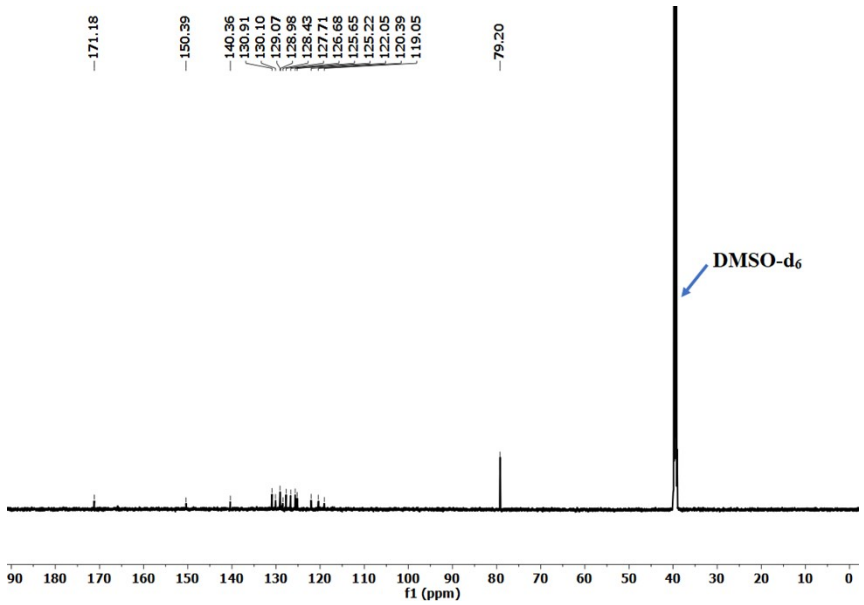


Figure S28: ^{13}CNMR (125 MHz, DMSO-d$_6$) spectra of the [Zn{34-ClATU)}$_2$·CHCl$_3$]

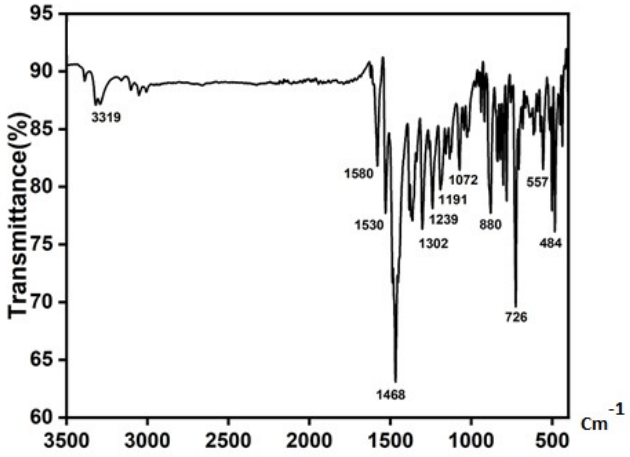
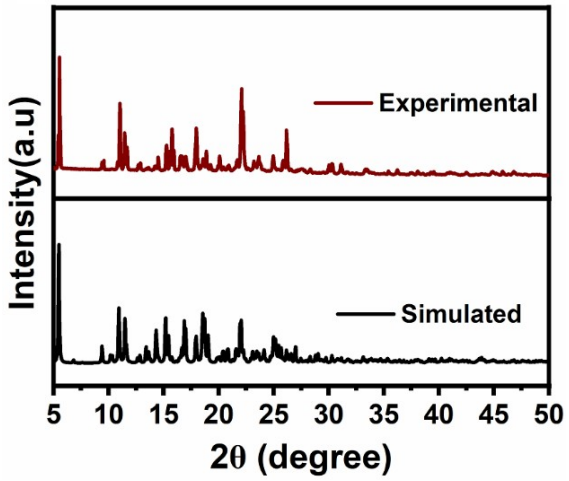
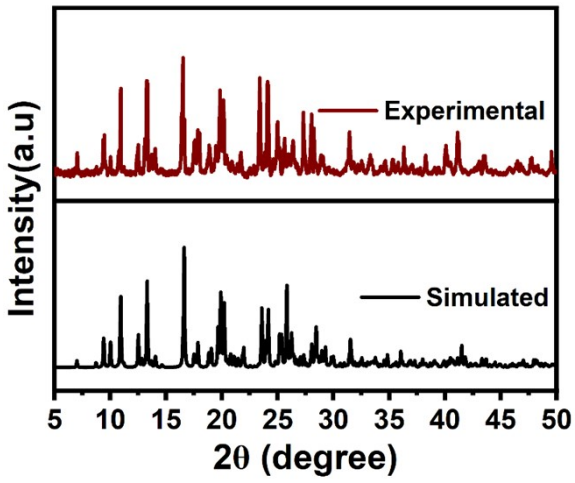


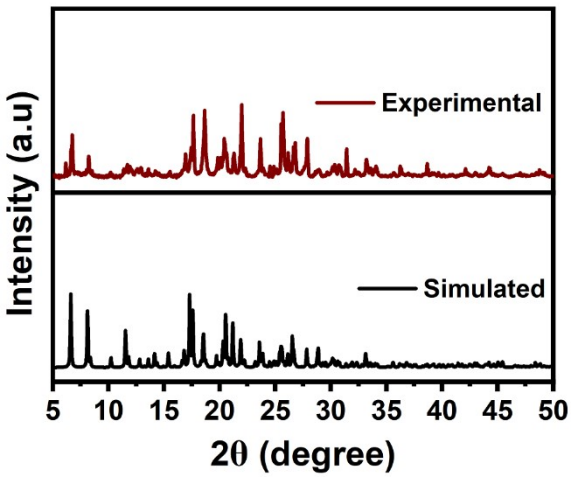
Figure S29: FT-IR spectrum (neat) of the [Zn{34-ClATU)}$_2$·CHCl$_3$]



(a)



(b)



(c)

Figure S30: Powder X-ray diffraction patterns of the (a) [Zn{4-OCH_3ATU)}$_2$·3DMF], (b) [Zn{23-ClATU)}$_2$·$CHCl_3$]-2, (c) [Zn{34-ClATU)}$_2$·$CHCl_3$]

Table S1: The crystal and refinement parameters of the ligands and the zinc complexes

Parameter	3-OCH_3HATU ·DMF	[Zn{3-OCH_3ATU)}$_2$ ·DMF]	4-OCH_3HATU	[Zn{4-OCH_3ATU)}$_2$· 3DMF]	34-ClHATU
Formula	$C_{27}H_{28}N_4SO_2$	$C_{52}H_{50}N_8O_4S_2Zn$	$C_{23}H_{19}N_3OS$	$C_{55}H_{57}N_9O_5S_2Zn$	$C_{22}H_{15}N_3Cl_2S$
Mol. wt.	472.59	980.49	385.47	1053.58	424.35
Space group	$P\,2_1/n$	$C2/c$	$P\,b\,c\,a$	$P\,\bar{1}$	$P\,2_1\,2_1\,2_1$
a(Å)	15.043(3)	31.105(3)	8.1754(6)	8.740(3)	4.4462(3)
b(Å)	7.2223(13)	9.3163(10)	19.3485(14)	16.268(6)	18.6620(14)
c (Å)	23.229(4)	19.108(2)	23.8411(18)	18.987(7)	22.7605(17)
α (°)	90	90	90	83.243(12)	90
β (°)	100.863(5)	118.737(3)	90	85.719(13)	90
γ (°)	90	90	90	85.156(13)	90
V (Å^3)	2478.5(8)	4855.3(9)	3771.2(5)	2665.6(17)	1888.6(2)
Density, g cm^{-3}	1.267	1.341	1.358	1.313	1.492
Abs. coeff., mm^{-1}	0.162	0.646	0.191	0.595	0.468
F(000)	1000	2048	1616	1104	874.07
Total no. of reflections	4391	4283	3327	9400	3348
Reflections, I > 2σ(I)	2478	3260	2428	7027	2210
Max. θ/°	25.048	25.047	25.038	25.050	25.040
Ranges (h, k, l)	$-17 \le h \le 17$ $-8 \le k \le 8$ $-27 \le l \le 27$	$-36 \le h \le 36$ $-11 \le k \le 11$ $-22 \le l \le 22$	$-9 \le h \le 9$ $-23 \le k \le 23$ $-28 \le l \le 28$	$-10 \le h \le 10$ $-19 \le k \le 19$ $-22 \le l \le 22$	$-5 \le h \le 5$ $-21 \le k \le 22$ $-26 \le l \le 27$
Complete to 2θ (%)	99.9	99.7	99.9	99.5	99.9
Data/restraints/parameters	4391/0/311	4283/0/306	3327/0/254	9400/5/657	3348/0/253
GooF (F^2)	1.024	1.188	1.036	1.014	1.176
R indices [I > 2σ(I)]	0.0658	0.0473	0.0425	0.0625	0.0642
wR_2 [I > 2σ(I)]	0.1601	0.1203	0.0998	0.1655	0.1084
R indices (all data)	0.1260	0.0756	0.0656	0.0839	0.1264
wR_2 (all data)	0.1944	0.1543	0.1105	0.1787	0.1401
CCDC No.	2346243	2346245	2346246	2346247	2346253

Parameter	23-ClHATU	[Zn{23-ClATU)}$_2$·$CHCl_3$]-1	[Zn{23-ClATU)}$_2$·$CHCl_3$]-2	[Zn{34-ClATU)}$_2$·$CHCl_3$]
Formula	$C_{22}H_{15}N_3Cl_2S$	$C_{46}H_{30}N_6Cl_{10}S_2Zn$	$C_{46}H_{30}N_6Cl_{10}S_2Zn$	$C_{46}H_{30}N_6S_2Cl_{10}Zn$
Mol. wt.	424.33	1150.75	1150.75	1150.75
Space group	$P\,2_1/n$	$P\,\bar{1}$	P ccn	$C2/c$
a(Å)	3.968(2)	9.909(5)	25.202(2)	24.961(6)
b(Å)	19.460(11)	15.867(9)	9.4183(9)	17.276(4)
c (Å)	25.084(13)	18.059(10)	20.248(2)	14.020(3)
α (°)	90	105.037(19)	90	90
β (°)	91.79(2)	97.95(2)	90	122.367(7)
γ (°)	90	103.998(19)	90	90
V (Å^3)	1936.2(19)	2599(3)	4806.2(8)	5106(2)
Density, g cm^{-3}	1.456	1.501	1.590	1.497
Abs. coeff., mm^{-1}	0.456	1.137	1.196	1.126
F(000)	872	1183	2320	2320
Total no. of reflections	3411	8862	4244	4481
Reflections, I > 2σ(I)	1805	5580	3771	3545
Max. θ/°	24.99	24.79	25.04	25.03
Ranges (h, k, l)	$-4 \le h \le 4$ $-18 \le k \le 23$ $-29 \le l \le 23$	$-11 \le h \le 11$ $-18 \le k \le 18$ $-21 \le l \le 21$	$-29 \le h \le 29$ $-11 \le k \le 11$ $-24 \le l \le 24$	$-29 \le h \le 29$ $-20 \le k \le 17$ $-15 \le l \le 16$
Complete to 2θ (%)	99.9	98.9	99.8	99.6
Data/restraints/parameters	3411/0/253	8862/0/550	4244/0/294	4481/0/294
GooF (F^2)	1.046	1.069	1.042	1.075
R indices [I > 2σ(I)]	0.0778	0.0734	0.0677	0.0773
wR_2 [I > 2σ(I)]	0.1701	0.2175	0.1734	0.2210
R indices (all data)	0.1621	0.1161	0.0755	0.0907
wR_2 (all data)	0.2131	0.2425	0.1827	0.2322
CCDC No.	2346248	2387524	2346250	2346254

Table S2: Hydrogen bond parameters of ligands and complexes

Compounds	D-H···A (Symmetry)	$d_{D\text{-}H}$ (Å)	$d_{H\cdots A}$ (Å)	$d_{D\cdots A}$ (Å)	∠D-H···A (o)
	N(2) -H(2) ···O(2) [1-x, 1-y, -z]	0.86	2.02	2.829(4)	157
3-OCH_3HATU·DMF	C(7) -H(7) ···S(1) [1/2+x, 1/2-y, 1/2+z]	0.93	2.75	3.654(4)	163
	C(15) -H(15) ···O(2) [1-x, 1-y, -z]	0.93	2.41	3.175(7)	139
	N(2) -H(2) ···S(1)) [-x, -y, -z]	0.86	2.62	3.4455(18)	162
4-OCH_3HATU	N(2) -H(2) ···O(1) [x, y, z]	0.93	2.35	2.973(7)	124
23-ClHATU	N(2) -H(2) …S(1) [2-x, 1-y, 1-z]	0.86	2.66	3.471(5)	157(4)
34-ClHATU	N(2) -H(2) …S(1) [-1/2+x, 1/2-y, 1-z]	0.86	2.73	3.5025(3)	149
	N(3) -H(3) …O(2) [x, y, z]	0.86	2.14	2.972(5)	163
[Zn{3-OCH_3ATU)}$_2$·	C(4) -H(4) ...O(1) [1/2-x, 5/2-y, 1-z]	0.93	2.56	3.259(8)	132
DMF]	C(22) -H(22) ...O(2) [x, y, z]	0.93	2.48	3.277(5)	144
	N(3) -H(3) …O(4) [-1+x, y, z]	0.86	2.01	2.844(10)	163
[Zn{4-OCH_3ATU)}$_2$·	N(6) -H(6) ...O(3) [-x, 1-y, 1-z]	0.86	2.06	2.918(5)	173
3DMF]	C(45) -H(45) …O(3) [-x, 1-y, 1-z]	0.93	2.59	3.373(7)	142
	C(49) -H(49A) …S(2) [-x, 1-y, 1-z]	0.93	2.81	3.536(5)	135

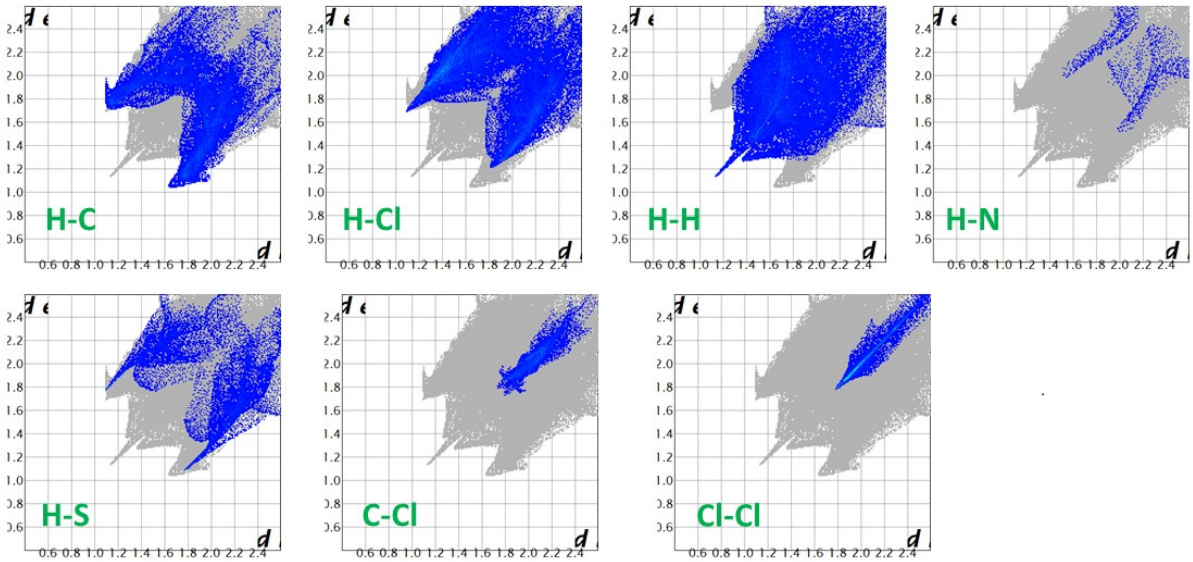


Figure S31: Finger-print plots of Hirshfeld surfaces with different contacts in [Zn{23-ClATU)}$_2$·CHCl$_3$]-1

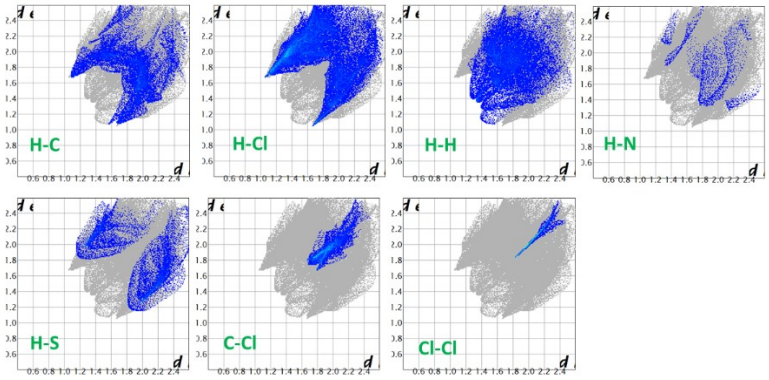
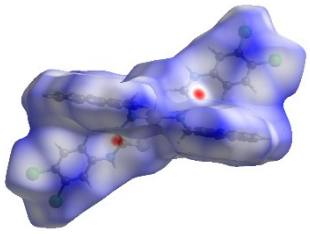
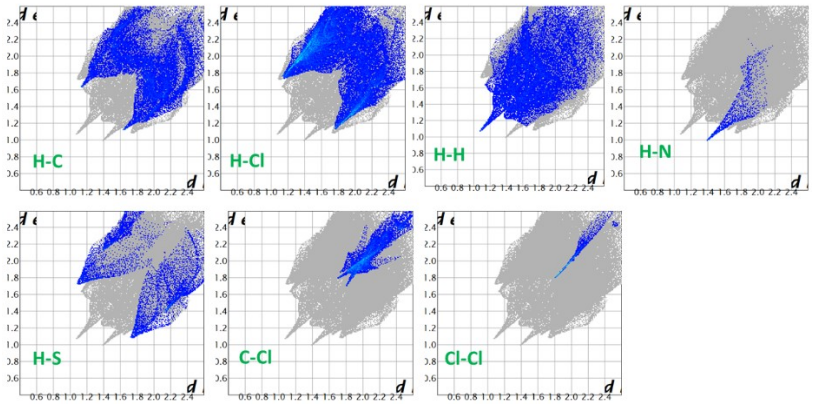


Figure S32: Finger-print plots of Hirshfeld surfaces with different contacts in [Zn{23-ClATU)}$_2$·CHCl$_3$]-2

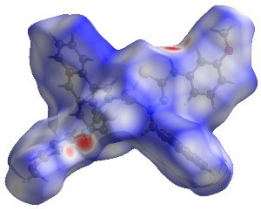


(a)

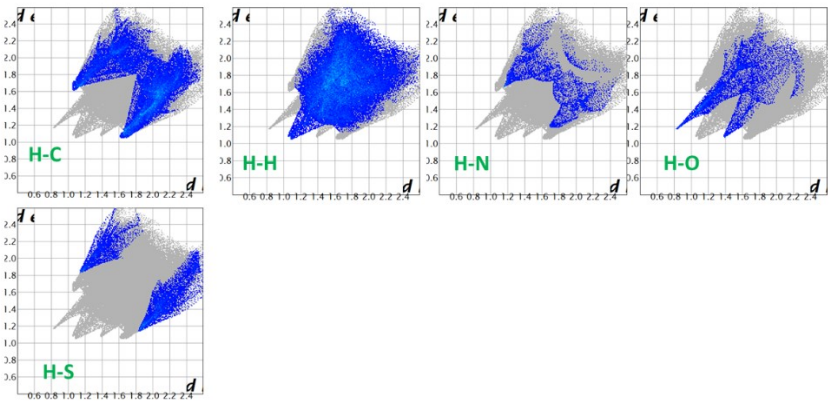


(b)

Figure S33: (a) Hirshfeld surface of [Zn{34-ClATU)}$_2$·CHCl$_3$], (b) Finger-print plots of different contacts [Zn{34-ClATU)}$_2$·CHCl$_3$]

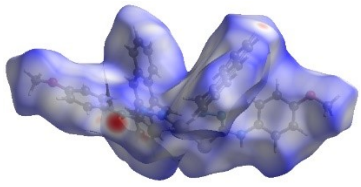


(a)

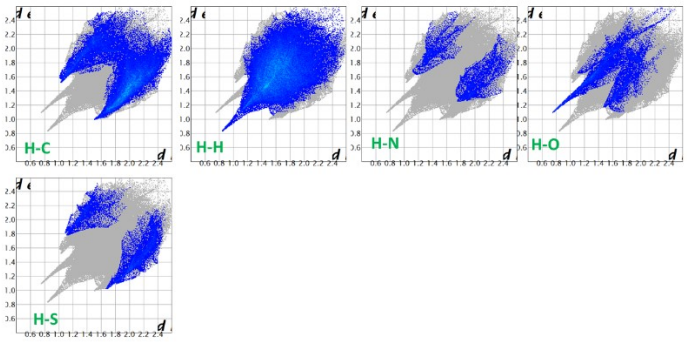


(b)

Figure S34: (a) Hirshfeld surface of [Zn{3-OCH$_3$ATU)}$_2$·DMF], (b) Finger-print plots of different contacts [Zn{3-OCH$_3$ATU)}$_2$·DMF]



(a)



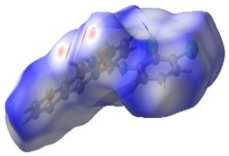
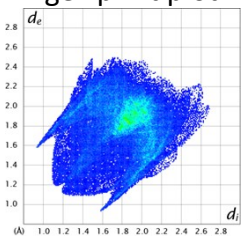
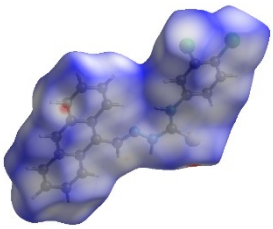
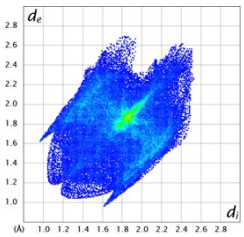
(b)

Figure S35: (a) Hirshfeld surface of [Zn{4-OCH_3ATU)}$_2$·3DMF], (b) Finger-print plots of different contacts [Zn{4-OCH_3ATU)}$_2$·3DMF]

Table S3 : The percentge contacts of different atoms within a radius of 3.8 Å from Finger-print plots of the complexes

Close Contacts (%) including reciprocal	[Zn{23-ClATU)}$_2$·$CHCl_3$]-1	[Zn{23-ClATU)}$_2$·$CHCl_3$]-2	[Zn{34-ClATU)}$_2$·$CHCl_3$]	[Zn{3-OCH_3ATU)}$_2$·DMF]	[Zn{4-OCH_3ATU)}$_2$·3DMF]
H-C	18.9 %	13.5%	18.2 %	24.6 %	26.1 %
H-Cl	26.7 %	32.8 %	34.6 %		
H-H	28.6 %	21.3 %	20.4 %	47.7 %	49.3 %
H-N	1.0 %	2.2 %	1.4 %	4.5 %	4.3 %
H-S	7.2 %	8.9 %	6.8 %	8.0 %	7.1 %
C-Cl	3.5 %	7.0 %	8.5 %	-	-
Cl-Cl	4.6 %	2.8 %	1.5 %	-	-
H-O	-	-	-	6.4 %	8.2 %

Table S4: Hershfeld surfaces, Finger-print plots and percentage contacts in the ligands

Hirshfeld surface	Finger-print plot	% of contacts
 23-ClHATU		C…H 8.6 %@ C…C 14.0 % C…S 0.3 % C…N 0.3 % C…Cl 1.3 5 % H…H 33.5 % Cl…Cl 1.0 % (without reciprocal)
 34-ClHATU		C…H 9.8 % C…C 10.5 % C…S 0.0 % C…O 0.3 % C…Cl 2.3 % C…N 1.7 % H…H 29.5 %

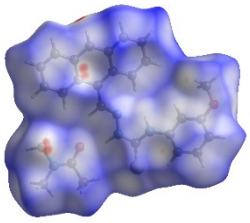
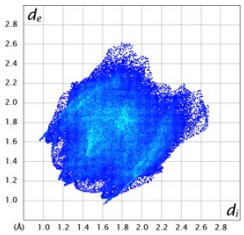
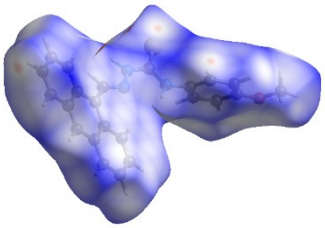
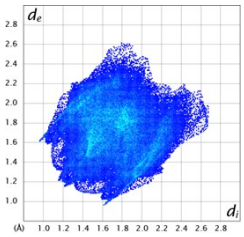
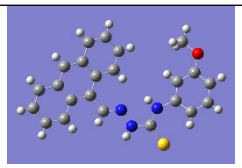
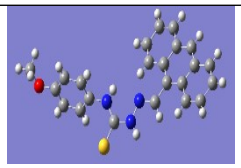
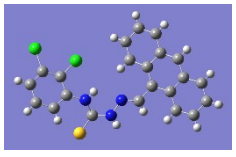
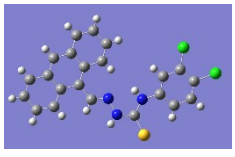
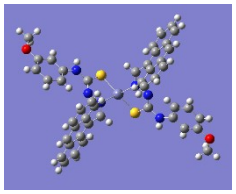
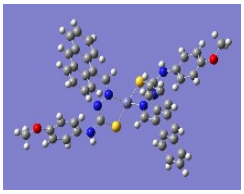
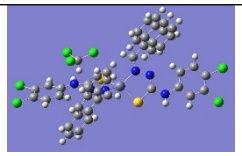
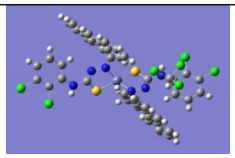
 3-OCH_3HATU·DMF		(without reciprocal) (with reciprocal) C…H 21.7 % C…C 4.9 % C…S 0.0 % H…H 50.2 % O…H 8.5 % S…H 7.4 %
 4-OCH_3HATU		(with reciprocal) C…H 22.7 % C…C 2.5 % C…S 0.3 % H…H 51.6 % O…H 11.1 % S…H 6.1 %

Table S5: The theoretical energy of the positional isomeric molecules and complexes calculated by DFT using B3LYP level with basis set LANL2DZ, singlet state without solvation

Energy of different positional isomers and compounds (in Hartee)		Difference Kcal/mol (within bracket are in Hartee)
		0.15 kcal/mol
3-OCH_3HATU -1136.834746	4-OCH_3HATU -1136.834990	(0.000244)
		27.42 kcal/mol
23-ClHATU -1051.062921	34-ClHATU -1051.106619	(0.043698)
		7.89 kcal/mol
$Zn\{3\text{-}OCH_3ATU)\}_2$ -2338.206190	$Zn\{4\text{-}OCH_3ATU)\}_2$ -2338.193609	(0.012581)

		144.50 kcal/mol
Zn{34-ClATU)}	$Zn\{23\text{-}ClATU)\}_2$-2	
-2250.091415	-2250.321696	(-0.230281)