New Journal of Chemistry

Supplementary Information

New amide based iridium(III) complexes: Synthesis, characterization, photoluminescence and DFT/TD-DFT studies

Cigdem Sahin[a,*], Aysen Goren[a], Serkan Demir [b] and Muhammet Serdar Cavus[c]

[a]*Department of Chemistry, Art&Science Faculty, Pamukkale University, Denizli, TURKEY*

[b]*Giresun University, Department of Industrial Engineering, 28200, Giresun, Turkey*

[c]*Kastamonu University, Department of Biomedical Engineering, Kastamonu, Turkey*

* cigdemsahin82@gmail.com

Figures SI:

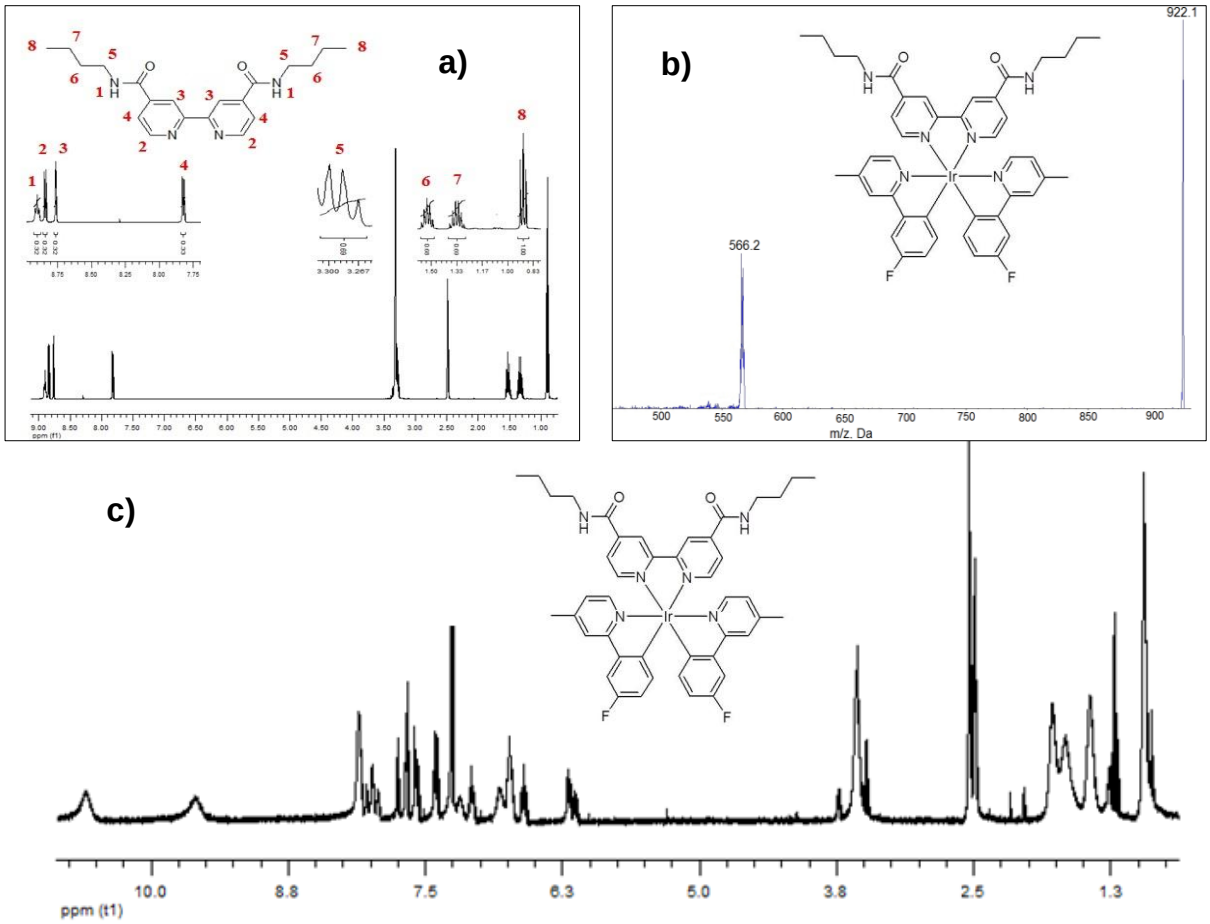

Figure S1. a) ^{1}H NMR spectrum of L_2 ligand in DMSO-d_6 b) ^{1}H NMR spectrum of complex 2 in $CDCl_3$ c) ESI mass spectra of complex 2 dissolved in acetonitrile.

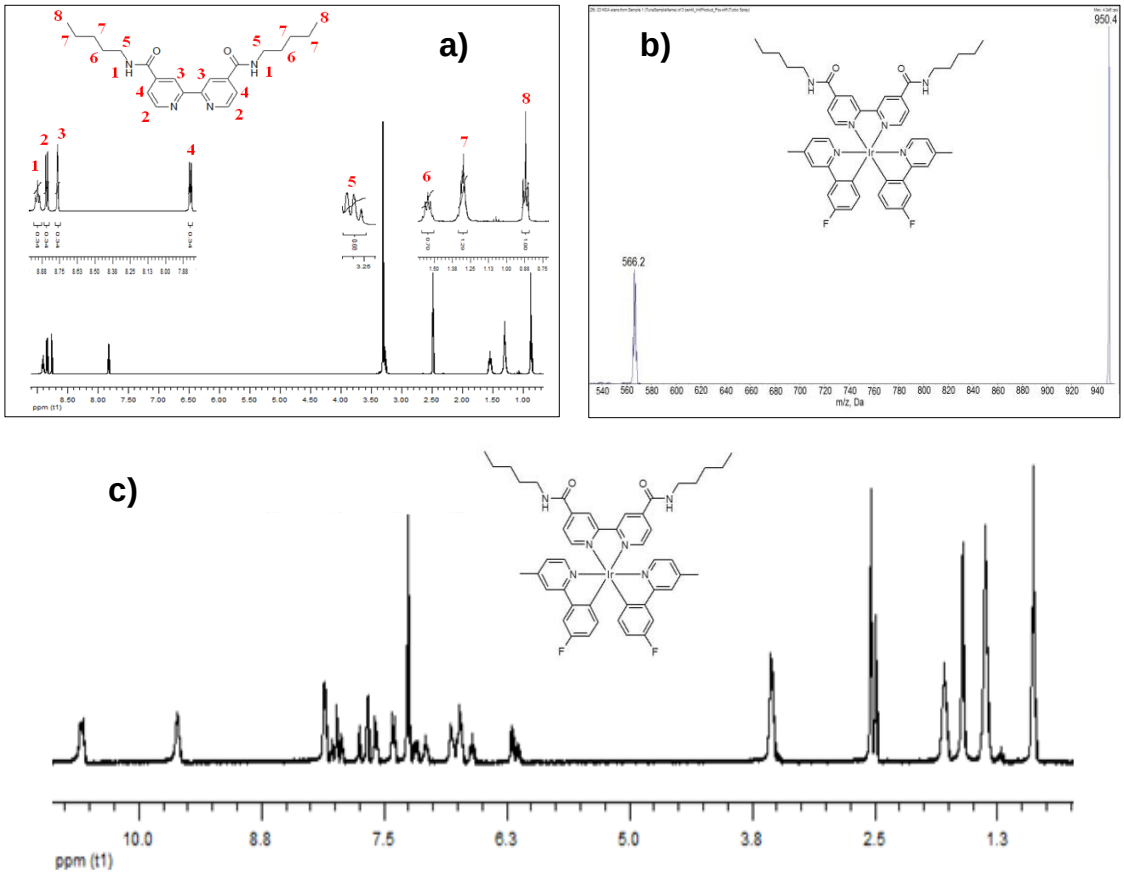

Figure S2. a) ^{1}H NMR spectrum of L_3 ligand in DMSO-d_6 b) ^{1}H NMR spectrum of complex 3 in $CDCl_3$ c) ESI mass spectra of complex 3 dissolved in acetonitrile.

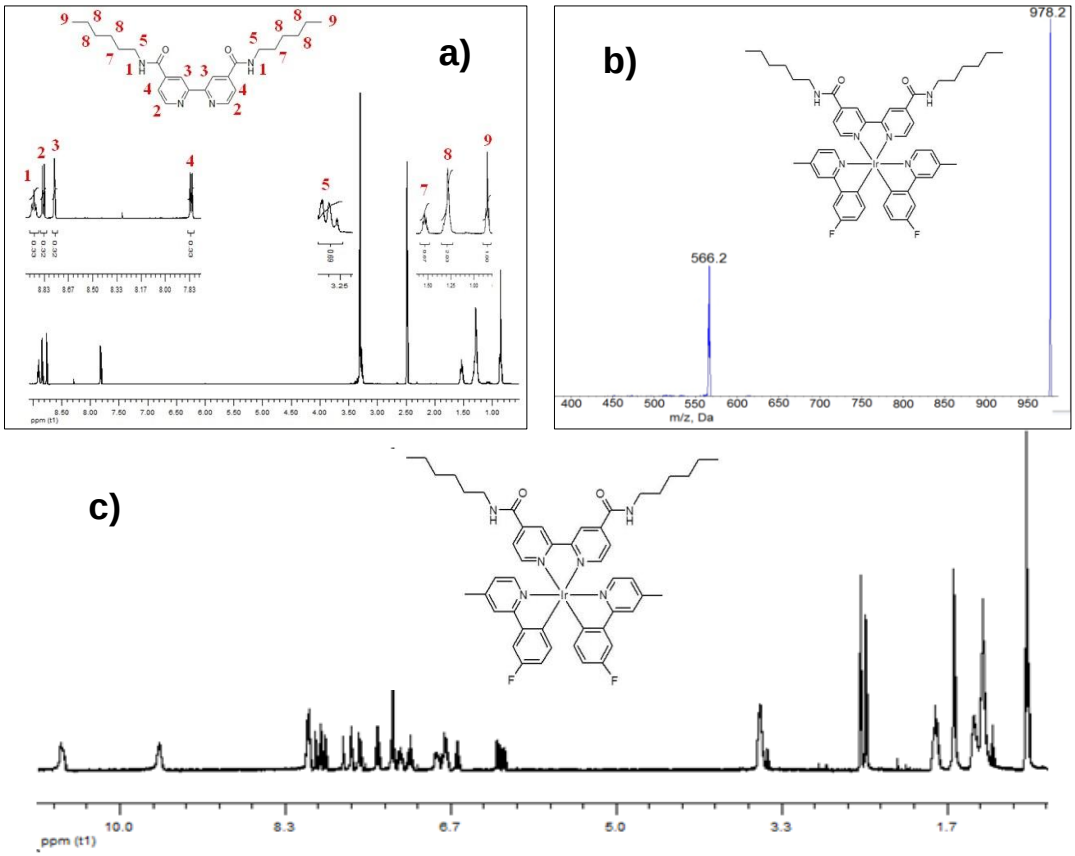

Figure S3. a) ^{1}H NMR spectrum of L_4 ligand in DMSO-d_6 b) ^{1}H NMR spectrum of complex 4 in $CDCl_3$ c) ESI mass spectra of complex 4 dissolved in acetonitrile.

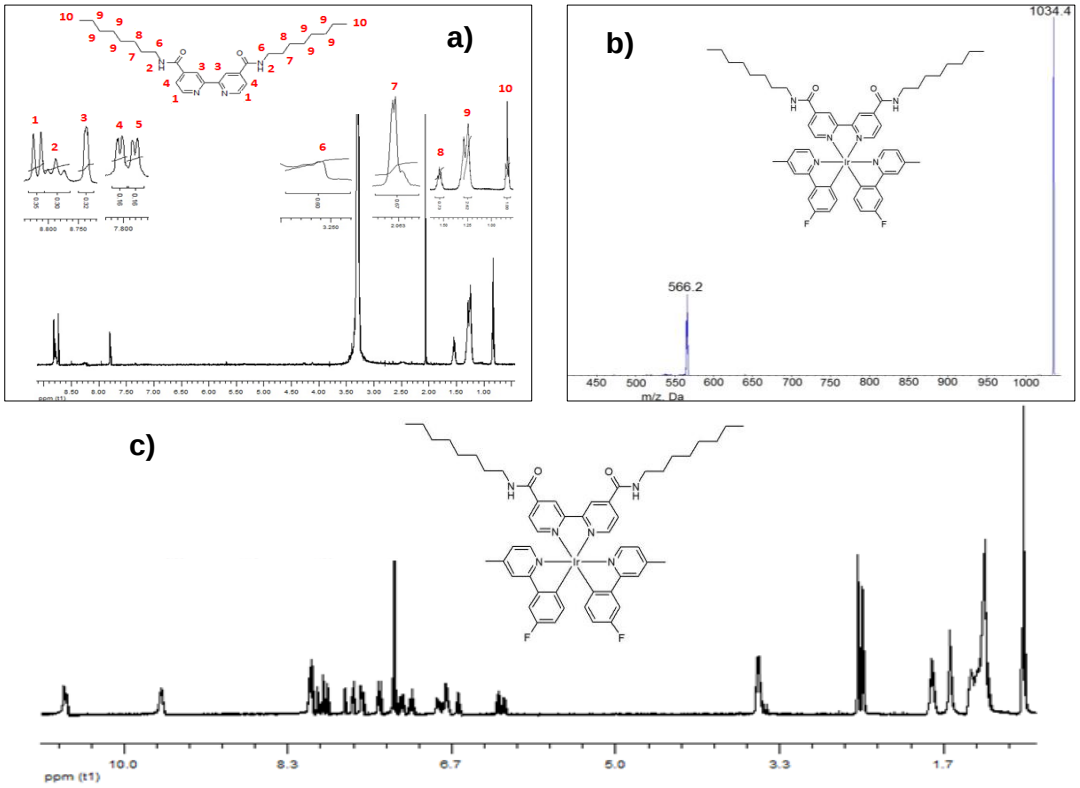

Figure S4. a) ^{1}H NMR spectrum of L_5 ligand in DMSO-d_6 b) ^{1}H NMR spectrum of complex 5 in $CDCl_3$ c) ESI mass spectra of complex 5 dissolved in acetonitril.

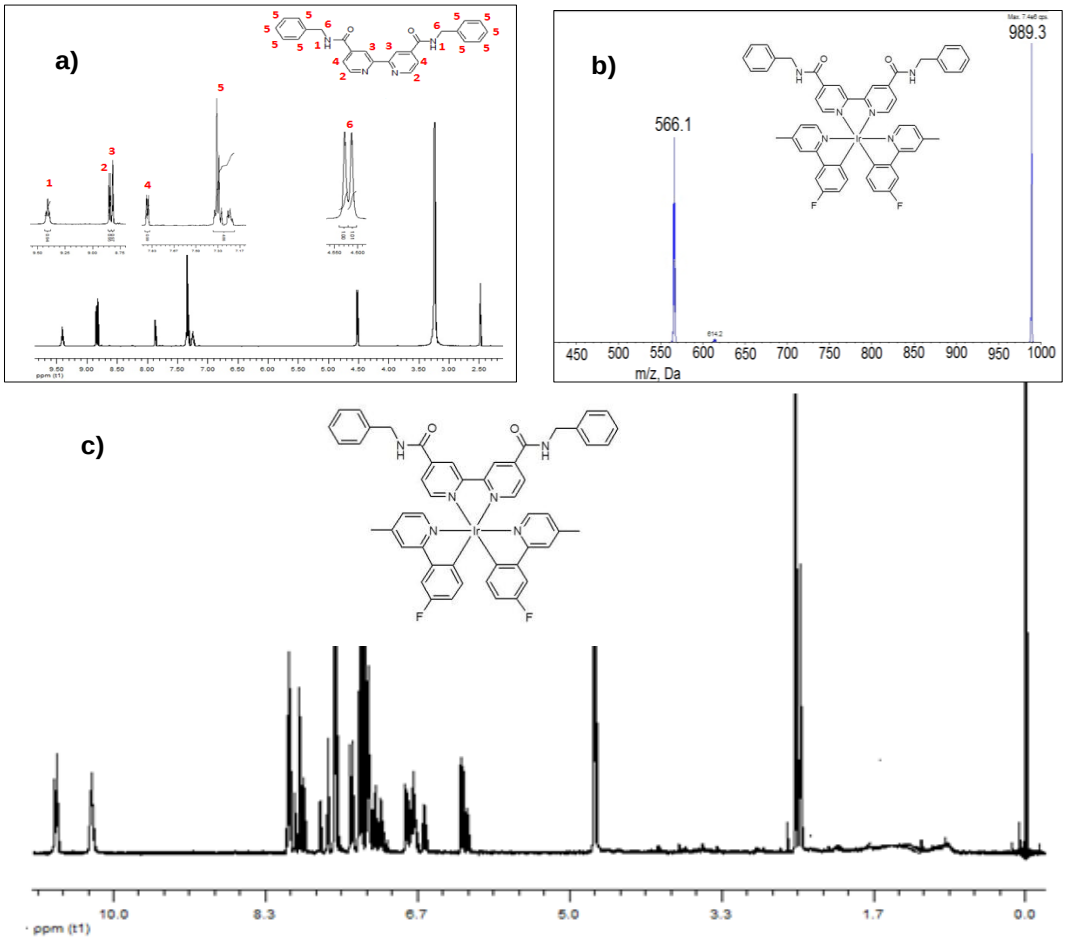

Figure S5. a) ^{1}H NMR spectrum of L_6 ligand in DMSO-d_6 b) ^{1}H NMR spectrum of complex 6 in $CDCl_3$ c) ESI mass spectra of complex 6 dissolved in acetonitrile.

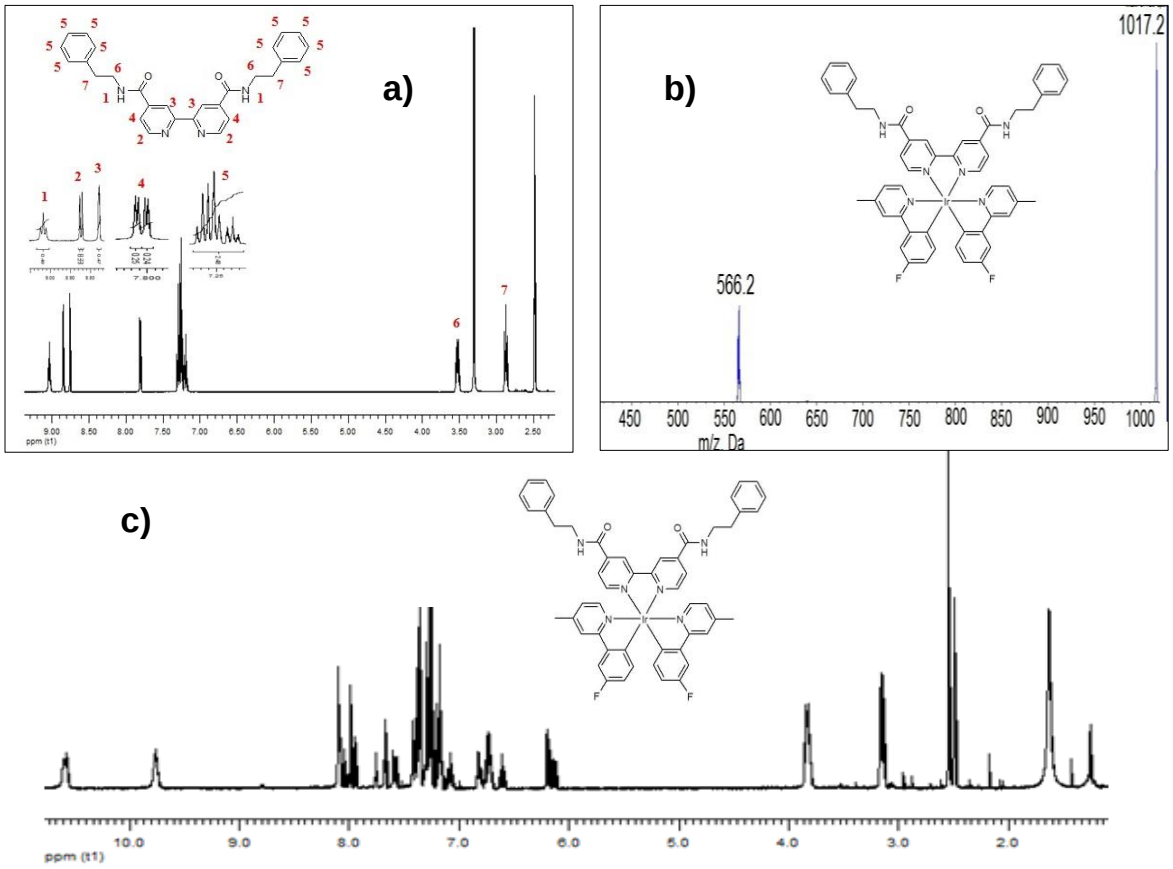

Figure S6. a) ^{1}H NMR spectrum of L_7 ligand in DMSO-d_6 b) ^{1}H NMR spectrum of complex 7 in $CDCl_3$ c) ESI mass spectra of complex 7 dissolved in acetonitrile.

The rationale for the choose of theory level and basis sets:

Since none of experimental reference geometry for the optimizations are available, the comparison for different functionals is not possible. Therefore we intuitively select the most popular B3LYP funtional for the optimizations considering the electronic structural properties of these type of compounds. All other energetic calculations were done by using CAM-B3LYP functional. More precisely and as given in the related reference in the manuscript, CAM-B3LYP functional gives good approximations for charge tansfer type and localized excitations which exist in our complexes since it predicts energies to the accuracy of B3LYP and to the accuracy of 0.1 eV for charge transfer transitions. The functional contains various exchange functionals contributions from 19% to 65% depending on the interelectron distances.

Nonetheless, whether the gap values can be more improved, The popular pure LSDA, LYP, M06L and hybrid B3P86 and M06-2X functionals were tested for SPE calculations. B3P86 and M06-2X functionals given absurd results and not regarded while the following results were obtained for pure functionals;

$HOMO\text{-}LUMO_{LSDA}$:-1.19 eV

$HOMO\text{-}LUMO_{LSDA(PCM)}$: -1.496 eV

$HOMO\text{-}LUMO_{LYP}$: -2.83 eV

$HOMO\text{-}LUMO_{LYP(PCM)}$: -3.22 eV

$HOMO\text{-}LUMO_{M06L:}$ -1.39 eV

$HOMO\text{-}LUMO_{M06L(PCM):}$ -1.73 eV

$HOMO\text{-}LUMO_{CAM\text{-}B3LYP}$: -2.91 eV

$HOMO\text{-}LUMO_{EXPT}$: -2.19 eV

pure LSDA functional underestimated the actual value about 1.0 eV and 0.7 eV for gas phase and PCM calculations respectively while pure M06L functional underestimated about 0.80 eV and 0.49 eV for gas-pahse and PCM calculations respectively. The only pure LYP functional slightly better estimated the actual value relative to CAM-B3LYP with an overestimation of 0.64 eV and 1.03 eV for gas-phase and PCM calculations respectively.

Nevertheless, for unity in terms of using one functional throught the calculations, we adopted only CAM-B3LYP functional since the difference between CAM-B3LYP and LYP calculations for HOMO-LUMO gap as given above is 0.08 eV. As we given the references for CAM-B3LYP functional in section 2.4., this functional gives good approximations for charge tansfer type and localized excitations which exist in our complexes since it predicts energies to the accuracy of B3LYP and to the accuracy of 0.1 eV for charge transfer transitions. The functional contains various exchange functionals contributions from 19% to 65% depending on the interelectron distances.

In terms of Basis sets, We thought that it is rational to use 3-21G* for H and F atoms in the calculations concerning the gain of computation time since the contribution of these atoms to the energetic quantities are almost quantitatively negligible. To crosscheck, we made three TD-DFT calculations for complex 1 by using 6-31G(d,p) for the atoms other than metal center and obtained following results for the transitions:

$S_0 \rightarrow T_1$(6-31G(d,p)): 473.55 nm (excitation)

$S_0 \rightarrow T_1$(3-21G*(H,F)): 473.48 nm (excitation)

$T_1 \rightarrow S_0$(6-31G(d,p)): 515 nm (emission)

$T_1 \rightarrow S_0$(3-21G*(H,F)): 521 nm (emission)

$T_1 \rightarrow S_0$(Expt.): 548 nm (emission)

$S_1 \rightarrow S_0$(6-31G(d,p): 504.07 nm

$S_1 \rightarrow S_0$(3-21G*(H,F)): 508.96 nm

The results obtained from the calculations where 6-31G(d,p) basis set was used for non-metal atoms did not change the results significantly. Even, TD-DFT calculation with 6-31G(d,p) for triplet emission resulted a more deviated value of 6 nm from experimental one.

Besides, in our calculations the number of basis functions are 834 while it is 965 in case of use of 6-31G(d,p) for non-metal atoms. The difference is 131 and may not be ignorable considering the $N^{\simeq 4}$ dependence of computation time for DFT calculations (N: number of basis functions) especially, considering relatively long computation time for excited state optimizations. Therefore, we used 3-21G* for relatively insignificant atoms for optimum time saving by avoiding significant change of energetic quantities. Eventually, we made about 20 seperate energy computations for all complexes in total and used 3-21G* basis set for H and F atoms of quantitatively negligible contributions to transition energies and molecular orbitals as well.

The cartesian coordinates for the optimizations of complex 1:

Ground state optimization:

1 1

Ir	0.00000000	0.00000000	1.14787000
C	-1.40725800	-0.11668800	2.61904100
C	-2.01359900	1.12604600	2.95300600
C	-1.84544000	-1.25951800	3.30987800
C	-1.51239500	2.28871200	2.22101200
C	-3.01907400	1.20523500	3.92801600
C	-2.84669800	-1.17821400	4.27853200
H	-1.39904100	-2.22498500	3.10150700
C	-1.92450900	3.61159700	2.40296700
C	-3.42449200	0.05268700	4.57712700
H	-3.49194900	2.14122600	4.19580800
H	-3.18205600	-2.05792200	4.81292500
C	0.00000000	3.00617300	0.54970200
C	-1.37088400	4.65328500	1.65532600
H	-2.68278600	3.82707700	3.14447000
C	-0.38660100	4.32695100	0.70860300
H	0.75882800	2.72317700	-0.16611000
H	0.07749900	5.09652500	0.10521900
N	-0.54092000	1.99964300	1.28446600
C	1.51239500	-2.28871200	2.22101200
C	0.00000000	-3.00617300	0.54970200
C	2.01359900	-1.12604600	2.95300600
C	1.92450900	-3.61159700	2.40296700
C	0.38660100	-4.32695100	0.70860300
H	-0.75882800	-2.72317700	-0.16611000
C	3.01907400	-1.20523500	3.92801600
C	1.37088400	-4.65328500	1.65532600
H	2.68278600	-3.82707700	3.14447000
H	-0.07749900	-5.09652500	0.10521900
C	1.84544000	1.25951800	3.30987800
C	3.42449200	-0.05268700	4.57712700
H	3.49194900	-2.14122600	4.19580800
C	2.84669800	1.17821400	4.27853200
H	1.39904100	2.22498500	3.10150700
H	3.18205600	2.05792200	4.81292500

C	1.40725800	0.11668800	2.61904100
N	0.54092000	-1.99964300	1.28446600
C	0.73253000	0.09604100	-1.78571700
C	2.65991700	0.39868800	-0.46366100
C	-0.73253000	-0.09604100	-1.78571700
C	1.50313000	0.17732200	-2.94919900
C	3.45740900	0.51400600	-1.59104400
H	3.05873900	0.47284000	0.53912700
C	-1.50313000	-0.17732200	-2.94919900
C	2.88145000	0.37128500	-2.85782800
H	1.03330500	0.11479100	-3.92028100
H	4.51508700	0.72650000	-1.51174400
C	-2.65991700	-0.39868800	-0.46366100
C	-2.88145000	-0.37128500	-2.85782800
H	-1.03330500	-0.11479100	-3.92028100
C	-3.45740900	-0.51400600	-1.59104400
H	-3.05873900	-0.47284000	0.53912700
H	-4.51508700	-0.72650000	-1.51174400
N	-1.31736700	-0.19932300	-0.55292200
N	1.31736700	0.19932300	-0.55292200
F	4.40773900	-0.12692800	5.52636000
F	-4.40773900	0.12692800	5.52636000
C	-1.82202200	6.08233400	1.86654600
H	-2.88854300	6.18534100	1.63448400
H	-1.67543000	6.38023900	2.91094800
H	-1.26215700	6.77135500	1.22935600
C	1.82202200	-6.08233400	1.86654600
H	2.88854300	-6.18534100	1.63448400
H	1.67543000	-6.38023900	2.91094800
H	1.26215700	-6.77135500	1.22935600
C	3.77971700	0.62583900	-4.04524400
O	4.71528900	1.43409200	-3.91849900
C	-3.77971700	-0.62583900	-4.04524400
O	-4.71528900	-1.43409200	-3.91849900
N	3.48489000	-0.01417100	-5.21840000
H	4.06816700	0.29362600	-5.99769300
N	-3.48489000	0.01417100	-5.21840000
H	-4.06816700	-0.29362600	-5.99769300
C	-2.86661100	1.35412500	-5.38553400
C	-3.88981200	2.38291600	-5.91352700
H	-2.01972800	1.28859700	-6.07977600
H	-2.49409400	1.68427100	-4.41334300
C	-3.23741700	3.76698900	-6.11171700
H	-4.29768400	2.02719700	-6.86818500
H	-4.72053100	2.45072100	-5.20211600
H	-3.97115000	4.48615900	-6.48765700
H	-2.84043000	4.15026600	-5.16449100
H	-2.41544800	3.71142200	-6.83440600
C	2.86661100	-1.35412500	-5.38553400
C	3.88981200	-2.38291600	-5.91352700
H	2.01972800	-1.28859700	-6.07977600
H	2.49409400	-1.68427100	-4.41334300
C	3.23741700	-3.76698900	-6.11171700
H	4.29768400	-2.02719700	-6.86818500

H	4.72053100	-2.45072100	-5.20211600
H	3.97115000	-4.48615900	-6.48765700
H	2.84043000	-4.15026600	-5.16449100
H	2.41544800	-3.71142200	-6.83440600

Excited state optimization (the coordinates obtained from the ground state optimization output):

1 1

Ir	0.00000000	0.00000000	1.18064500
C	-1.42139200	-0.12666200	2.63084300
C	-2.04741800	1.11620300	2.95911500
C	-1.86310500	-1.28202200	3.31664700
C	-1.54337300	2.28450100	2.22803200
C	-3.07332700	1.19703700	3.92978800
C	-2.88394800	-1.22056600	4.28390600
H	-1.40954400	-2.24702400	3.11112900
C	-1.97777100	3.61570500	2.39871500
C	-3.46441700	0.02272400	4.56535100
H	-3.56080400	2.12897600	4.19817000
H	-3.22215100	-2.10497400	4.81574000
C	0.00000000	3.00919000	0.58360900
C	-1.41675100	4.66883500	1.65772200
H	-2.75554600	3.82717500	3.12438100
C	-0.39950300	4.33673700	0.72748500
H	0.78314100	2.73514700	-0.11170900
H	0.07954100	5.10479900	0.12806300
N	-0.55184300	1.99652800	1.30994000
C	1.54337300	-2.28450100	2.22803200
C	0.00000000	-3.00919000	0.58360900
C	2.04741800	-1.11620300	2.95911500
C	1.97777100	-3.61570500	2.39871500
C	0.39950300	-4.33673700	0.72748500
H	-0.78314100	-2.73514700	-0.11170900
C	3.07332700	-1.19703700	3.92978800
C	1.41675100	-4.66883500	1.65772200
H	2.75554600	-3.82717500	3.12438100
H	-0.07954100	-5.10479900	0.12806300
C	1.86310500	1.28202200	3.31664700
C	3.46441700	-0.02272400	4.56535100
H	3.56080400	-2.12897600	4.19817000
C	2.88394800	1.22056600	4.28390600
H	1.40954400	2.24702400	3.11112900
H	3.22215100	2.10497400	4.81574000
C	1.42139200	0.12666200	2.63084300
N	0.55184300	-1.99652800	1.30994000
C	0.73518400	0.09545800	-1.75594600
C	2.66439400	0.40868500	-0.43057900
C	-0.73518400	-0.09545800	-1.75594600
C	1.51249900	0.15723200	-2.92844200
C	3.47717900	0.51330000	-1.56349100
H	3.06896900	0.49493300	0.57032600
C	-1.51249900	-0.15723200	-2.92844200
C	2.89942200	0.36997100	-2.84195900

H	1.04137000	0.06462900	-3.89955700
H	4.53692800	0.72097500	-1.46599200
C	-2.66439400	-0.40868500	-0.43057900
C	-2.89942200	-0.36997100	-2.84195900
H	-1.04137000	-0.06462900	-3.89955700
C	-3.47717900	-0.51330000	-1.56349100
H	-3.06896900	-0.49493300	0.57032600
H	-4.53692800	-0.72097500	-1.46599200
N	-1.32030300	-0.20946800	-0.51827500
N	1.32030300	0.20946800	-0.51827500
F	4.48139000	-0.08884500	5.52727200
F	-4.48139000	0.08884500	5.52727200
C	-1.86003100	6.10165500	1.84746600
H	-2.72453900	6.17427600	2.51437000
H	-1.05053400	6.70477800	2.28020300
H	-2.12825800	6.56341200	0.88885900
C	1.86003100	-6.10165500	1.84746600
H	2.72453900	-6.17427600	2.51437000
H	1.05053400	-6.70477800	2.28020300
H	2.12825800	-6.56341200	0.88885900
C	3.78240100	0.59822600	-4.04959300
O	4.61981000	1.53967600	-4.00700800
C	-3.78240100	-0.59822600	-4.04959300
O	-4.61981000	-1.53967600	-4.00700800
N	3.63614600	-0.20037100	-5.15623400
H	4.23325900	0.07532500	-5.93371000
N	-3.63614600	0.20037100	-5.15623400
H	-4.23325900	-0.07532500	-5.93371000
C	-2.94123300	1.49841900	-5.29562200
C	-3.79069000	2.49502300	-6.11270000
H	-1.96969300	1.36206200	-5.79611200
H	-2.74882300	1.91340400	-4.29973000
C	-3.06582200	3.84225200	-6.30689400
H	-4.01671700	2.05730300	-7.09675700
H	-4.75128100	2.65156600	-5.60372500
H	-3.68315300	4.53204000	-6.89337900
H	-2.85228200	4.32411600	-5.34326100
H	-2.11468700	3.71173400	-6.84023800
C	2.94123300	-1.49841900	-5.29562200
C	3.79069000	-2.49502300	-6.11270000
H	1.96969300	-1.36206200	-5.79611200
H	2.74882300	-1.91340400	-4.29973000
C	3.06582200	-3.84225200	-6.30689400
H	4.01671700	-2.05730300	-7.09675700
H	4.75128100	-2.65156600	-5.60372500
H	3.68315300	-4.53204000	-6.89337900
H	2.85228200	-4.32411600	-5.34326100
H	2.11468700	-3.71173400	-6.84023800