Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information:

Tuning the Electronic and Photophysical Properties of Heteroleptic Iridium (III) Phosphorescent Emitters through Ancillary Ligand Substitution: A Theoretical Perspective

Huifang Li, Paul Winget, Chad Risko, John Sears, and Jean-Luc Brédas*

School of Chemistry and Biochemistry & Center for Organic Photonics and Electronics
Georgia Institute of Technology
Atlanta, Georgia 30332-0400

Table S1. HOMO and LUMO energies in the ground state of the FIracac and analogs as well as their corresponding triplet energies calculated at the (U)B3LYP/[LANL2DZ-ECP/6-31G(d,p)] level of theory. VE ≡ vertical T_1 energy; AE ≡ adiabatic T_1 energy; VIP ≡ vertical ionization potentials (ΔE for the reaction A(g) → $A^+(g) + e^-(g)$ where $A^+(g)$ is computed using the optimal A(g) geometry); VEA ≡ vertical electron affinities (ΔE for the reaction A(g) → $A^-(g) + e^-(g)$ where $A^-(g)$ is computed using the optimal A(g) geometry).

		S_0		ΔSCF				
		HOMO	LUMO	VE	AE[a]	AE[b]	VIP	VEA
FIracac	**A**	-5.30	-1.52	2.9	2.5	2.48	6.5	-0.26
	B	-5.25	-1.49	2.8	2.6	2.56	6.4	-0.24
	C	-5.34	-1.48	2.9	2.7	2.62	6.5	-0.23
FIrmfac	**A**	-5.58	-1.67	2.6	2.2	2.15	6.8	-0.46
	B	-5.45	-1.66	3.0	2.7	2.58	6.6	-0.45
	C	-5.56	-1.64	2.9	2.6	2.57	6.7	-0.42
	D	-5.57	-1.65	2.9	2.4	2.33	6.9	-0.43
FIrdbm	**A**	-5.30	-1.72	2.4	2.1	2.05	6.4	-0.57
	B	-5.27	-1.71	2.8	2.3	2.23	6.4	-0.56
	C	-5.34	-1.72	2.5	2.2	2.17	6.4	-0.56
FIrpfac	**A**	-5.56	-1.98	2.4	2.0	1.97	6.7	-0.69
	B	-5.44	-1.94	2.8	2.2	2.22	6.6	-0.68
	C	-5.53	-1.96	2.5	2.2	2.13	6.7	-0.67
	D	-5.55	-1.96	2.5	2.2	2.15	6.7	-0.68
FIrnatfac	**A**	-5.58	-2.00	2.4	2.0	1.99	6.7	-0.75
	B	-5.45	-1.99	2.6	2.2	2.19	6.6	-0.76
	C	-5.56	-1.97	2.5	2.2	2.12	6.6	-0.74
	D	-5.56	-2.00	2.5	2.2	2.13	6.7	-0.76

[a] Energies without ZPVE correction. [b] Energies with ZPVE correction. The same is true for Table S2 and S3.

Table S2. HOMO and LUMO energies in the ground state of the FIrpic and analogs as well as their corresponding triplet energies calculated at the (U)B3LYP/[LANL2DZ-ECP/6-31G(d,p)] level of theory.

		S_0		ΔSCF				
		HOMO	**LUMO**	**VE**	**AE**[a]	**AE**[b]	**VIP**	**VEA**
FIrpic	**A**	-5.57	-1.81	3.02	2.49	2.40	6.81	-0.59
	B	-5.47	-1.74	2.94	2.68	2.57	6.68	-0.52
	C	-5.54	-1.76	2.99	2.73	2.61	6.78	-0.53
	D	-5.58	-1.77	2.94	2.74	2.66	6.80	-0.53
FIrmpic	**A**	-5.53	1.78	3.04	2.53	2.45	6.76	-0.56
	B	-5.50	-1.70	2.94	2.69	2.58	6.71	-0.52
	C	-5.48	-1.71	2.95	2.79	2.67	6.70	-0.51
	D	-5.60	-1.72	2.94	2.66	2.53	6.81	-0.51
FIrfpic	**A**	-5.74	-2.24	2.90	2.26	2.19	6.97	-0.88
	B	-5.61	-2.24	2.89	2.64	2.55	6.82	-0.83
	C	-5.70	-2.24	2.94	2.44	2.36	6.93	-0.85
	D	-5.74	-2.26	2.93	2.66	2.54	6.94	-0.85
FIrprz	**A**	-5.78	-2.31	2.85	2.24	2.17	7.02	-0.90
	B	-5.64	-2.32	2.87	2.60	2.51	6.86	-0.84
	C	-5.74	-2.33	2.90	2.41	2.33	6.98	-0.86
	D	-5.77	-2.34	2.91	2.67	2.54	6.99	-0.85
FIriq	**A**	-5.53	-2.14	2.67	2.15	2.09	6.72	-0.84
	B	-5.42	-2.15	2.90	2.52	2.44	6.60	-0.80
	C	-5.49	-2.14	2.87	2.40	2.29	6.68	-0.81
	D	-5.54	-2.18	2.76	2.38	2.27	6.71	-0.82

Table S3. HOMO and LUMO energies in the ground state of the FIrppz and analogs as well as their corresponding triplet energies calculated at the (U)B3LYP/[LANL2DZ-ECP/6-31G(d,p)] level of theory.

		S_0		ΔSCF				
		HOMO	**LUMO**	**VE**	**AE[a]**	**AE[b]**	**VIP**	**VEA**
FIrppz	**A**	-5.19	-1.64	2.92	2.62	2.48	6.42	-0.38
	B	-5.40	-1.58	3.04	2.73	2.61	6.58	-0.36
	C	-5.26	-1.57	2.94	2.69	2.56	6.46	-0.35
	D	-5.35	-1.59	2.98	2.71	2.58	6.58	-0.35
FIrmppz	**A**	-5.05	-1.63	2.81	2.53	2.39	6.28	-0.37
	B	-5.29	-1.56	3.05	2.73	2.61	6.48	-0.35
	C	-5.14	-1.55	2.86	2.60	2.48	6.34	-0.34
	D	-5.18	-1.57	3.03	2.60	2.48	6.43	-0.34
FIrfppz	**A**	-5.51	-1.79	3.04	2.73	2.59	6.70	-0.55
	B	-5.57	-1.73	3.07	2.73	2.62	6.77	-0.54
	C	-5.54	-1.72	3.06	2.77	2.64	6.72	-0.53
	D	-5.64	-1.73	3.16	2.71	2.59	6.82	-0.52
FIrptz	**A**	-5.61	-1.78	3.17	2.78	2.66	6.81	-0.52
	B	-5.54	-1.71	3.06	2.73	2.62	6.74	-0.50
	C	-5.58	-1.70	3.07	2.78	2.66	6.8	-0.50
	D	-5.62	-1.72	3.14	2.70	2.58	6.82	-0.49

Table S4. Comparison of selected bond lengths for the isolated ancillary proligands and in the Ir complexes in the S_0 state, obtained at the B3LYP/[LANL2DZ-ECP/6-31G(d,p)] level of theory, for the O^O, O^N and N^N series.

	Ancillary Proligands		Ancillary Ligand in Complexes			
	O3-C[a]	**O3'-C**[b]	**O3-C**	**O3'-C**	**Ir-O3**[c]	**Ir-O3'**[d]
O^O						
FIracac	1.325	1.252	1.275	1.275	2.192	2.192
FIrmfac	1.317	1.249	1.269	1.269	2.194	2.207
FIrdbm	1.324	1.262	1.278	1.279	2.184	2.184
exp.[h]					2.121	2.149
FIrpfac	1.322	1.250	1.272	1.270	2.190	2.202
FIrnatfac	1.322	1.250	1.271	1.271	2.187	2.205
O^N						
FIrpic	1.346	1.340	1.295	1.350	2.180	2.206
exp.[g]					2.124	2.126
FIrmpic	1.347	1.338	1.293	1.355	2.158	2.298
FIrfpic	1.344	1.339	1.293	1.349	2.183	2.206
FIrprz	1.345	1.339	1.295	1.347	2.186	2.199
FIriq	1.347	1.323	1.293	1.336	2.160	2.204
N^N						
FIrppz	1.342	1.349	1.335	1.367	2.141	2.235
FIrmppz	1.344	1.349	1.335	1.368	2.140	2.235
FIrfppz	1.336	1.348	1.330	1.366	2.145	2.238
FIrptz	1.343	1.348	1.328	1.366	2.148	2.244

[a,b] The bond label in the N^N series corresponds to C-N3 or C-N3'. [b] It corresponds to C-N3' in the O^N series. [c,d] The bond label in the N^N series corresponds to Ir-N3 or Ir-N3'. [d] It corresponds to Ir-N3' in the O^N series.

Table S5. Variation in selected bond-length parameters for the Ir complexes for the the lowest triplet state compared to the ground state, obtained at the B3LYP/[LANL2DZ-ECP/6-31G(d,p)] level of theory.

	$\Delta d(T_1\text{-}S_0)$					
	Ir-X3[a]	**Ir-X3'**[a]	**Ir-N1**	**Ir-C1**	**Ir-N2**	**Ir-C2**
O^O						
FIracac	-0.009	0.003	0.025	0.027	-0.019	0.001
FIrmfac	0.001	-0.016	0.025	0.027	-0.017	0.003
FIrdbm	0.071	0.064	0.007	-0.013	-0.014	-0.017
FIrpfac	0.080	0.096	0.008	-0.017	-0.015	-0.019
FIrnatfac	0.070	0.089	0.002	-0.014	-0.007	-0.016
O^N						
FIrpic	0.014	-0.046	-0.016	0.011	0.018	0.028
FIrmpic	0.006	-0.050	-0.016	0.006	0.022	0.032
FIrfpic	0.141	0.018	-0.009	-0.015	-0.012	-0.012
FIrprz	0.141	0.020	-0.009	-0.014	-0.010	-0.010
FIriq	0.128	0.010	-0.005	-0.015	-0.017	-0.014
N^N						
FIrppz	-0.009	-0.029	-0.015	0.008	0.026	0.027
FIrmppz	-0.008	-0.030	-0.015	0.008	0.026	0.027
FIrfppz	-0.010	-0.030	-0.014	0.009	0.027	0.027
FIrptz	-0.007	-0.032	-0.014	0.009	0.026	0.026

[a] X = O or N depending on the ancillary ligand.

Table S6. HOMO and LUMO energies in the ground state of the cyclometalating and ancillary proligands used for the heteroleptic Ir complexes discussed here as well as their corresponding vertical IPs and EAs calculated at the B3LYP/[LANL2DZ-ECP/6-31G(d,p)] level of theory.

	HOMO	LUMO	VIP	VEA
dfppy	-6.27	-1.25	8.04	0.48
O^O				
acac	-6.46	-1.11	8.82	1.09
mfac	-7.08	-2.04	9.44	0.20
dbm	-6.75	-2.47	7.80	-0.46
pfac	-6.19	-2.00	8.57	-0.67
natfac	-6.24	-2.43	7.87	-0.79
O^N				
pic	-7.09	-1.63	9.30	0.45
mpic	-6.97	-1.53	9.19	0.49
fpic	-7.49	-2.10	9.64	-0.09
prz	-7.06	-2.14	9.30	-0.01
iq	-6.42	-2.08	8.28	-0.28
N^N				
ppz	-6.14	-1.25	8.04	0.62
mppz	-6.04	-1.19	7.88	0.64
fppz	-6.59	-1.58	8.43	0.25
ptz	-6.59	-1.57	8.51	0.32

[a] All energies are in eV. [b] VEAs are defined as the energy change in the process $M+e^- \rightarrow M^{\cdot -}$, where negative values indicate exoergicity upon reduction of a molecule.

Table S7. HOMO and LUMO energies in the ground state of the heteroleptic Ir complexes as well as their vertical IPs and EAs calculated at the B3LYP/[LANL2DZ-ECP/6-31G(d,p)] level of theory.

	S_0(Complexes)					
	HOMO	**LUMO**	**VIP**	**VEA**	**AIP**	**AEA**
				O^O		
FIracac	-5.25	-1.49	6.4	-0.24	6.39	-0.36
FIrmfac	-5.45	-1.66	6.6	-0.45	6.60	-0.54
FIrdbm	-5.27	-1.71	6.4	-0.56	6.31	-0.73
FIrpfac	-5.44	-1.94	6.6	-0.68	6.54	-0.89
FIrnatfac	-5.45	-1.99	6.6	-0.76	6.53	-1.00
				O^N		
FIrpic	-5.47	-1.74	6.6	-0.52	6.55	-0.60
			6.6	-0.68[a]		
FIrmpic	-5.50	-1.70	6.7	-0.51	6.61	-0.61
FIrfpic	-5.61	-2.24	6.8	-0.83	6.69	-1.03
FIrprz	-5.64	-2.32	6.8	-0.84	6.72	-1.00
FIriq	-5.42	-2.15	6.6	-0.80	6.47	-0.97
				N^N		
FIrppz	-5.40	-1.58	6.5	-0.36	6.47	-0.44
FIrmppz	-5.29	-1.56	6.4	-0.35	6.35	-0.43
FIrfppz	-5.57	-1.73	6.7	-0.54	6.66	-0.61
FIrptz	-5.54	-1.71	6.7	-0.50	6.63	-0.58

[a] Values from Ref. 53.

Table S8. Contribution to the frontier MOs in the ground state of the heteroleptic Ir complexes, obtained using Mulliken population analysis at B3LYP/[LANL2DZ-ECP/6-31G(d,p)] level of theory.

	HOMO				LUMO			
	Ir	***dfppy***	***dfppy***	**ancillary**	**Ir**	***dfppy***	***dfppy***	**ancillary**
O^O								
FIracac	0.59	0.16	0.16	0.05	0.05	0.47	0.47	0.02
FIrmfac	0.46	0.16	0.17	0.04	0.04	0.29	0.48	0.22
FIrdbm	0.58	0.16	0.16	0.06	0.02	0.03	0.05	0.91
FIrpfac	0.45	0.16	0.17	0.05	0.03	0.03	0.05	0.91
FIrnatfac	0.41	0.16	0.17	0.05	0.03	0.03	0.03	0.91
O^N								
FIrpic	0.46	0.16	0.18	0.06	0.02	0.18	0.05	0.75
FIrmpic	0.48	0.17	0.16	0.05	0.04	0.35	0.13	0.48
FIrfpic	0.43	0.16	0.19	0.06	0.03	0.02	0.02	0.95
FIrprz	0.45	0.16	0.19	0.06	0.05	0.02	0.02	0.93
FIriq	0.48	0.16	0.18	0.06	0.02	0.02	0.01	0.87
N^N								
FIrppz	0.49	0.12	0.21	0.09	0.05	0.87	0.04	0.06
FIrmppz	0.48	0.04	0.04	0.47	0.05	0.87	0.04	0.05
FIrfppz	0.44	0.14	0.24	0.03	0.04	0.78	0.04	0.16
FIrptz	0.38	0.14	0.24	0.05	0.05	0.81	0.03	0.12

Table S9. NPA charges changes for the ligands obtained at B3LYP/[LANL2DZ-ECP/6-31G(d,p)] level of theory.

	S_0		T_1	
	q(a) [a]	**q(d)** [b]	**q(a)**	**q(d)**
O^O				
FIracac	-0.424	0.067	-0.405	0.041
FIrmfac	-0.459	0.103	-0.447	0.083
FIrdbm	-0.437	0.074	-0.656	0.295
FIrpfac	-0.463	0.103	-0.750	0.395
FIrnatfac	-0.465	0.107	-0.728	0.371
O^N				
FIrpic	-0.384	0.086	-0.353	0.075
FIrmpic	-0.389	0.087	-0.381	0.062
FIrfpic	-0.402	0.104	-0.825	0.515
FIrprz	-0.408	0.110	-0.827	0.516
FIriq	-0.381	0.080	-0.760	0.449
N^N				
FIrppz	-0.333	0.085	-0.327	0.069
FIrmppz	-0.330	0.082	-0.324	0.065
FIrfppz	-0.357	0.108	-0.352	0.094
FIrptz	-0.356	0.111	-0.350	0.094

[a] q(a) indicates the charge on the ancillary ligand. [b] q(d) indicates the charge on the 2-*dfppys*.

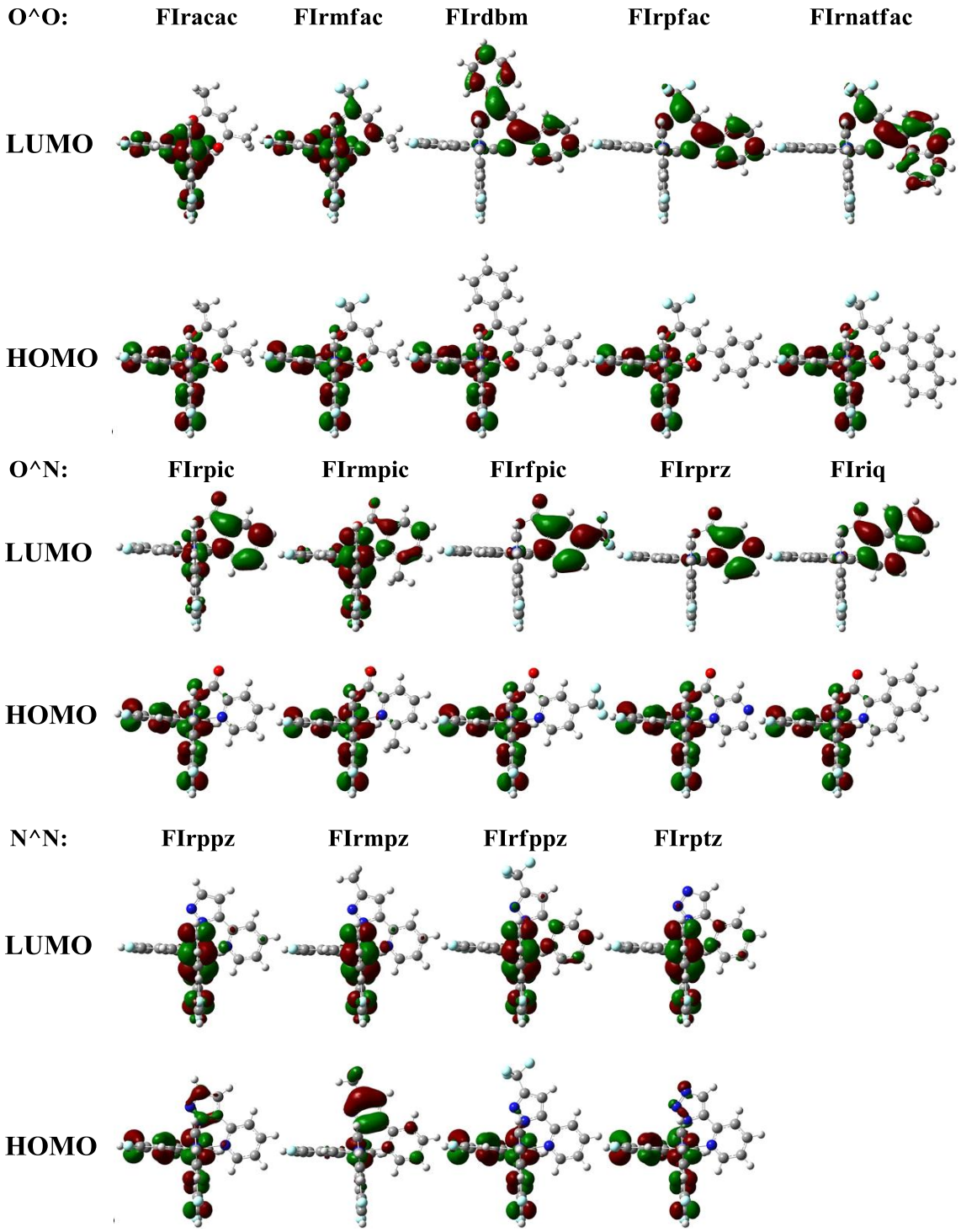

Figure S1. Representations of the HOMO and LUMO wave functions as determined at the B3LYP/[LANL2DZ-ECP/6-31G(d,p)] level of theory.

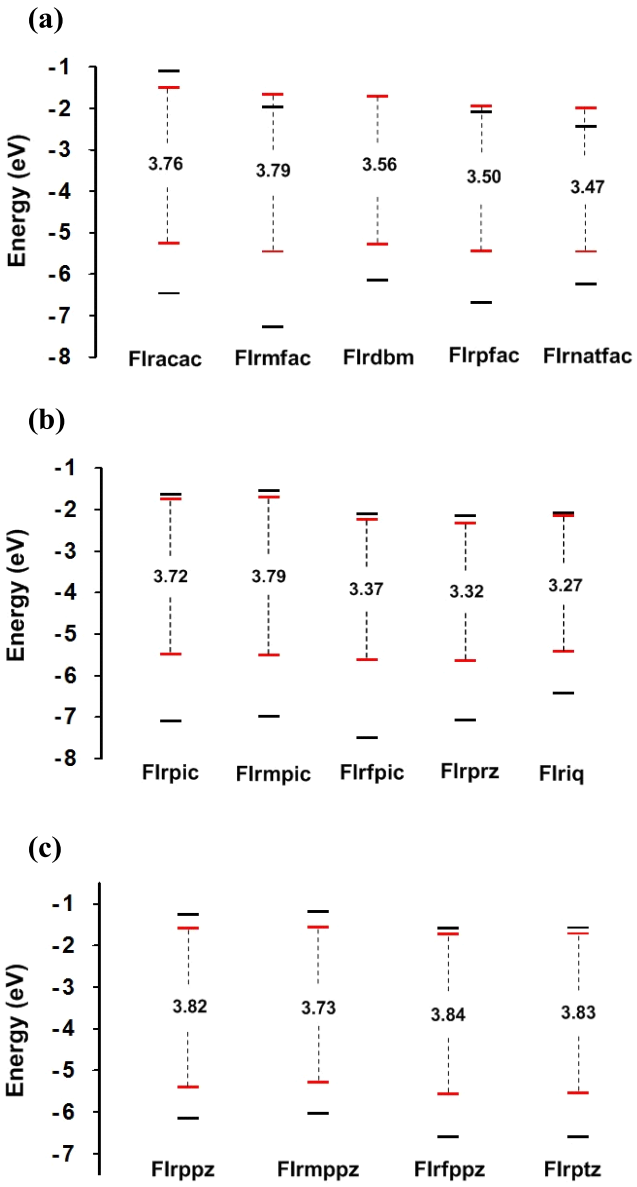

Figure S2. Comparison of the energies of the frontier molecular orbitals for the isolated proligands (black lines) and in the corresponding iridium complexes (red lines) in the S_0 state as determined at the B3LYP/[LANL2DZ-ECP/6-31G(d,p)] level of theory.

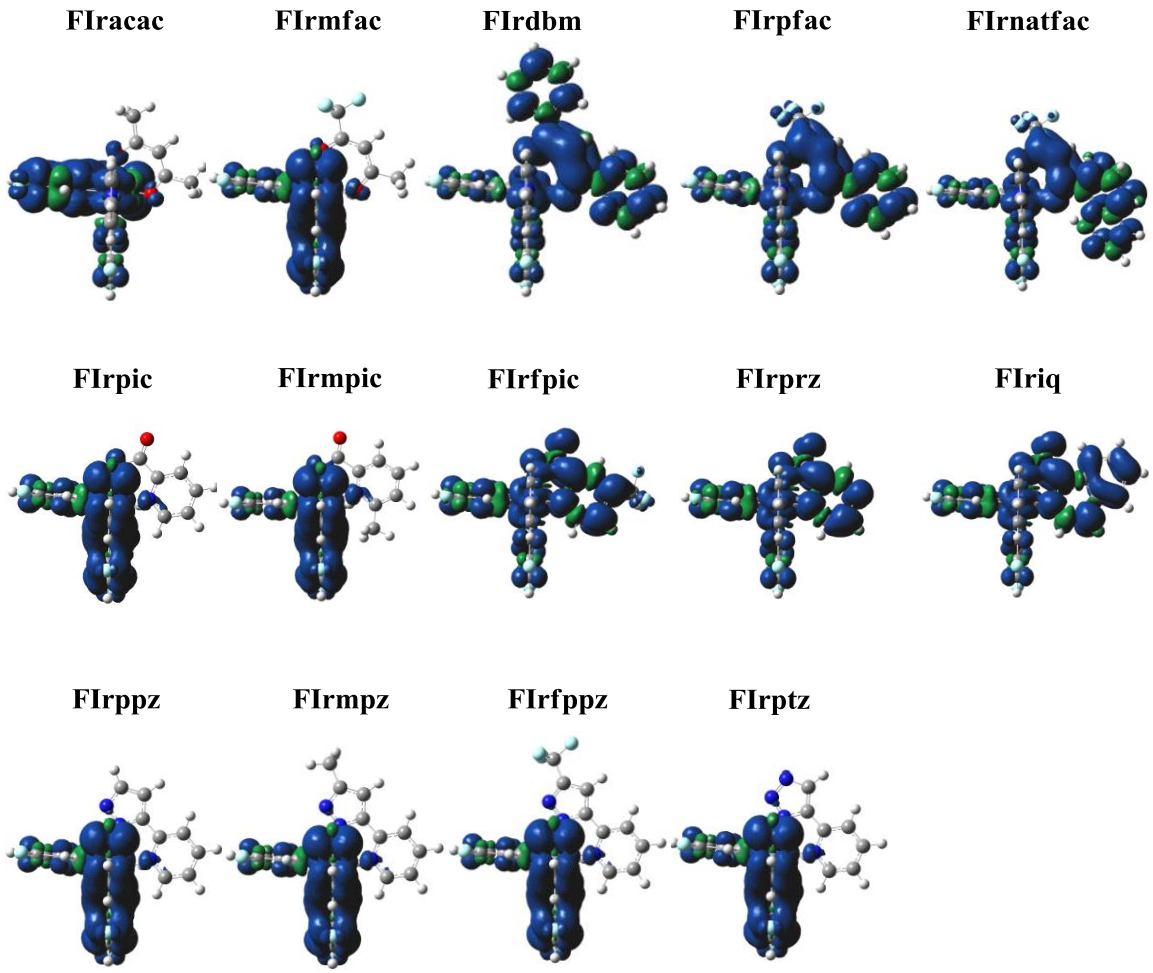

Figure S3. Representations of the spin density in the optimized triplet state as determined at the B3LYP/[LANL2DZ-ECP/6-31G(d,p)] level of theory.