Supporting Information

Hole/electron reorganization energies can be respectively expressed as:

$$\lambda_h = \lambda_+ + \lambda_0 = [E^+(M) - E^+M^+)] + [E(M^+) - E(M)]$$
$$= [E^+(M) - E(M)] - [E^+(M^+) - E(M^+)]) = IP_V - HEP^{1,2} \quad (1)$$

$$\lambda_e = \lambda_- + \lambda_0 = [E^-(M) - E^-(M^-)] + [E(M^-) - E(M)]$$
$$= [E(M^-) - E^-(M^-)] - [E(M) - E^-(M)]) = EEP - EA_V^{1,2} \quad (2)$$

Here E(M), $E^+(M^+)$ and $E^-(M^-)$ represent the energies of optimized neutral, cationic and anionic molecules, respectively. $E(M^+)/E(M^-)$ denote the energies of neutral species at the cationic/anionic geometries. $E^+(M)/E^-(M)$ denote the energies of cationic/anionic species at the neutral geometries. IP_V and EA_V are vertical ionization potential and electron affinity, respectively. HEP/EEP are hole/electron extraction potential. The meanings of all the parameters are shown in Figure S1.

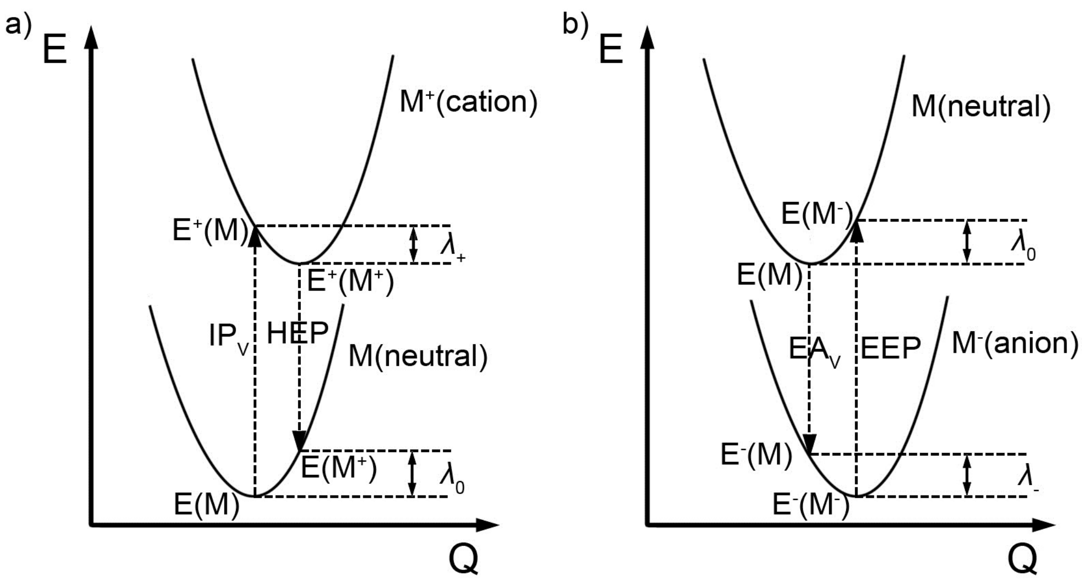


Figure S1. Potential energy surfaces of the neutral states and ionic states together with the compositions of the hole(a)/electron(b) internal reorganization energies.

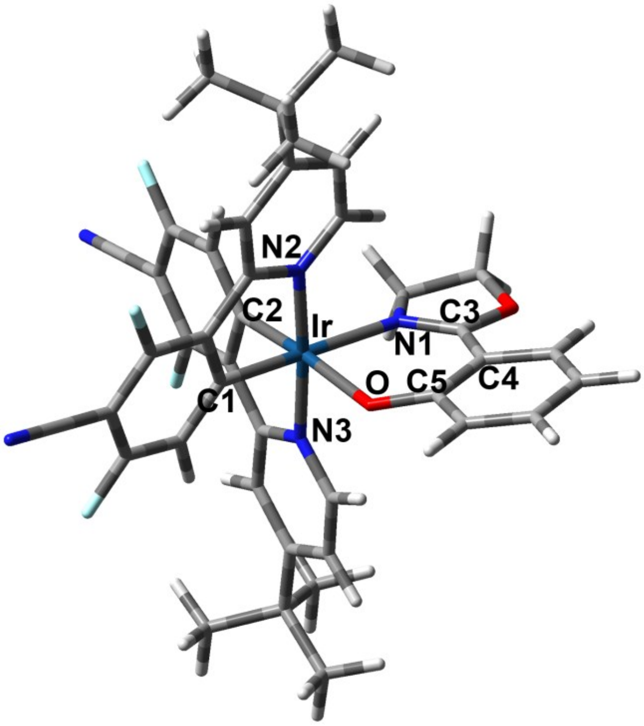


Fig. S2 Geometry structure of **1a** obtained from the single crystal data**.**

Table S1 Selected bond lengths (Å), bond angels (°), dihedral angle (°) and HOMO energy level of **1a** at S_0 state calculated by different functionals compared with the experimental values of the X-ray diffraction crystal structure, together with their difference (Δ).

	Expt.	PBE	TPSS	B3LYP	M062X	ΔPBE	ΔTPSS	ΔB3LYP	ΔM062X
Ir-O	2.108	2.164	2.150	2.159	2.171	0.056	0.042	0.051	0.062
Ir-N1	2.120	2.164	2.163	2.182	2.180	0.043	0.042	0.062	0.060
Ir-N2	2.042	2.053	2.059	2.072	2.066	0.012	0.017	0.031	0.024
Ir-C1	2.003	2.003	2.010	2.012	1.986	0.000	0.007	0.010	-0.016
Ir-N3	2.026	2.045	2.050	2.061	2.053	0.019	0.024	0.035	0.027
Ir-C2	1.988	1.994	2.004	2.006	1.978	0.006	0.016	0.018	-0.010
7O-1Ir-8N	87.0	85.7	85.8	84.9	84.1	-1.4	-1.3	-2.1	-3.0
N2-Ir-C1	80.9	80.6	80.4	80.3	80.7	-0.3	-0.5	-0.6	-0.2
N3-1Ir-C2	80.9	80.8	80.6	80.5	80.9	-0.1	-0.3	-0.5	0.0
N1-C3-C4-C5	4.7	11.7	11.4	11.4	16.5	7.1	6.7	6.8	11.8
E_{HOMO}	-5.55	-4.58	-4.61	-5.32	-6.59	0.97	0.94	0.23	-1.04

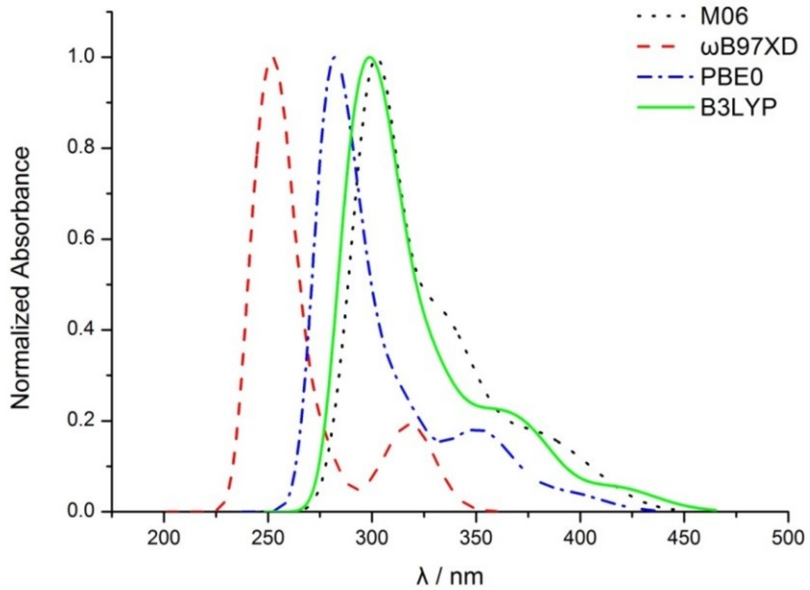


Fig. S3 Absorption spectra of **1a** simulated by TD-DFT with different functionals.

Table S2 The experimental absorption peaks (λ/nm) of **1a**.

λ	280	326	373

Table S3 Emission wavelength (λ/nm) of **1a** calculated by TD-DFT/TDA with different functionals, along with the experimental value.

	Expt.	B3LYP	PBE0	CAM-B3LYP	ωB97XD
λ	480	529	519	493	487

Table S4 Calculated efficient hole/electron transfer integral V_h/V_e (eV) and mobility k_h/k_e (s^{-1}) of the dimers composed of adjacent molecules. D (Å) is the centroid to centroid distance (Ir-Ir) of **1a**.

Pathway	D	V_h	k_h	V_e	k_e
1	12.72	0.00001	2.33E-02	0.00044	5.47E-03
2	14.57	0.00001		0.00417	
3	10.76	0.00006		-0.00018	
4	7.09	-0.00339		-0.00463	
5	10.16	-0.00088		-0.00037	
6	12.72	-0.01444		-0.01382	
7	11.53	0.00348		-0.00039	
8	13.41	-0.00987		0.00008	
9	12.78	-0.00007		0.00003	
10	10.98	0.00081		0.00000	
11	11.81	-0.00013		0.00068	
12	14.74	0.00000		-0.00001	

13	10.98	0.00081		0.00000

Table S5 Selected bond lengths (Å), bond angels (°) and dihedral angles (°) in optimized S_0 and T_1 with their difference (Δ) for **1a-3d** at the B3LYP/LANL2DZ/6-31G** level.

	S_0	T_1	Δ	S_0	T_1	Δ	S_0	T_1	Δ	S_0	T_1	Δ
		1a			**1b**			**2a**			**2b**	
Ir-O	2.159	2.168	0.009	2.172	2.161	-0.011	2.158	2.194	0.036	2.160	2.156	-0.004
Ir-N1	2.182	2.143	-0.039	2.188	2.126	-0.061	2.180	2.157	-0.022	2.179	2.164	-0.015
Ir-N2	2.072	2.079	0.006	2.058	2.056	-0.002	2.074	2.073	0.001	2.072	2.100	0.028
Ir-C1	2.012	2.025	0.013	2.005	2.003	-0.003	2.013	2.021	0.009	2.012	2.016	0.003
Ir-N3	2.061	2.058	-0.003	2.070	2.078	0.008	2.060	2.058	-0.002	2.060	2.032	-0.028
Ir-C2	2.006	2.001	-0.005	2.012	2.030	0.018	2.006	1.996	-0.010	2.005	1.997	-0.009
7O-Ir-N1	84.9	84.7	-0.2	83.2	84.6	1.4	84.8	85.3	0.6	85.2	83.8	-1.3
N2-Ir-C1	80.3	80.0	-0.3	80.6	80.5	0.0	80.3	80.2	-0.1	80.3	80.1	-0.2
N3-Ir-C2	80.5	80.5	0.0	80.3	80.0	-0.3	80.5	80.5	0.1	80.5	81.6	1.2
N1-C3-C4-C5	11.4	9.2	-2.3	-33.8	-21.9	11.9	13.1	11.4	-1.8	12.6	17.2	4.6
		2c			**2d**			**3a**			**3b**	
Ir-O	2.155	2.174	0.020	2.153	2.170	0.018	2.163	2.154	-0.009	2.168	2.164	-0.004
Ir-N1	2.181	2.159	-0.022	2.181	2.156	-0.024	2.187	2.184	-0.003	2.185	2.170	-0.016
Ir-N2	2.072	2.072	0.000	2.071	2.073	0.002	2.077	2.080	0.003	2.075	2.077	0.003
Ir-C1	2.012	2.021	0.010	2.011	2.022	0.011	2.014	2.020	0.006	2.012	2.021	0.009
Ir-N3	2.060	2.059	-0.001	2.061	2.059	-0.002	2.061	2.066	0.005	2.062	2.066	0.003
Ir-C2	2.007	1.999	-0.008	2.005	1.997	-0.008	2.001	1.998	-0.003	2.004	2.001	-0.003
7O-Ir-N1	85.0	85.5	0.5	82.1	84.3	2.2	84.2	83.5	-0.7	84.7	84.8	0.1
N2-Ir-C1	80.3	80.2	-0.1	80.3	80.1	-0.1	80.3	80.2	-0.1	80.2	80.1	-0.1
N3-Ir-C2	80.4	80.5	0.1	80.5	80.5	0.0	80.7	80.6	0.0	80.5	80.4	0.0
N1-C3-C4-C5	13.0	10.0	-2.9	22.9	15.8	-7.0	7.5	6.3	-1.2	10.8	8.2	-2.6
		3c			**3d**							
Ir-O	2.173	2.146	-0.027	2.192	2.207	0.015						
Ir-N1	2.186	2.165	-0.021	2.186	2.163	-0.023						
Ir-N2	2.074	2.069	-0.006	2.075	2.081	0.006						
Ir-C1	2.013	2.024	0.011	2.011	2.022	0.011						
Ir-N3	2.063	2.072	0.009	2.061	2.065	0.003						
Ir-C2	2.003	2.005	0.002	2.002	1.997	-0.006						
7O-Ir-N1	84.9	85.3	0.4	83.0	83.6	0.6						
N2-Ir-C1	80.3	80.1	-0.1	80.4	80.3	-0.1						
N3-Ir-C2	80.5	80.2	-0.3	80.6	80.6	0.0						
N1-C3-C4-C5	10.1	2.7	-7.4	35.0	37.0	2.0						

Table S6 Absorption wavelengths (λ/nm), excitation energies (E/eV), oscillator strengths (f) and the dominant configurations[a] for major $S_0 \rightarrow S_n$ transitions calculated by TDDFT/PBE0.

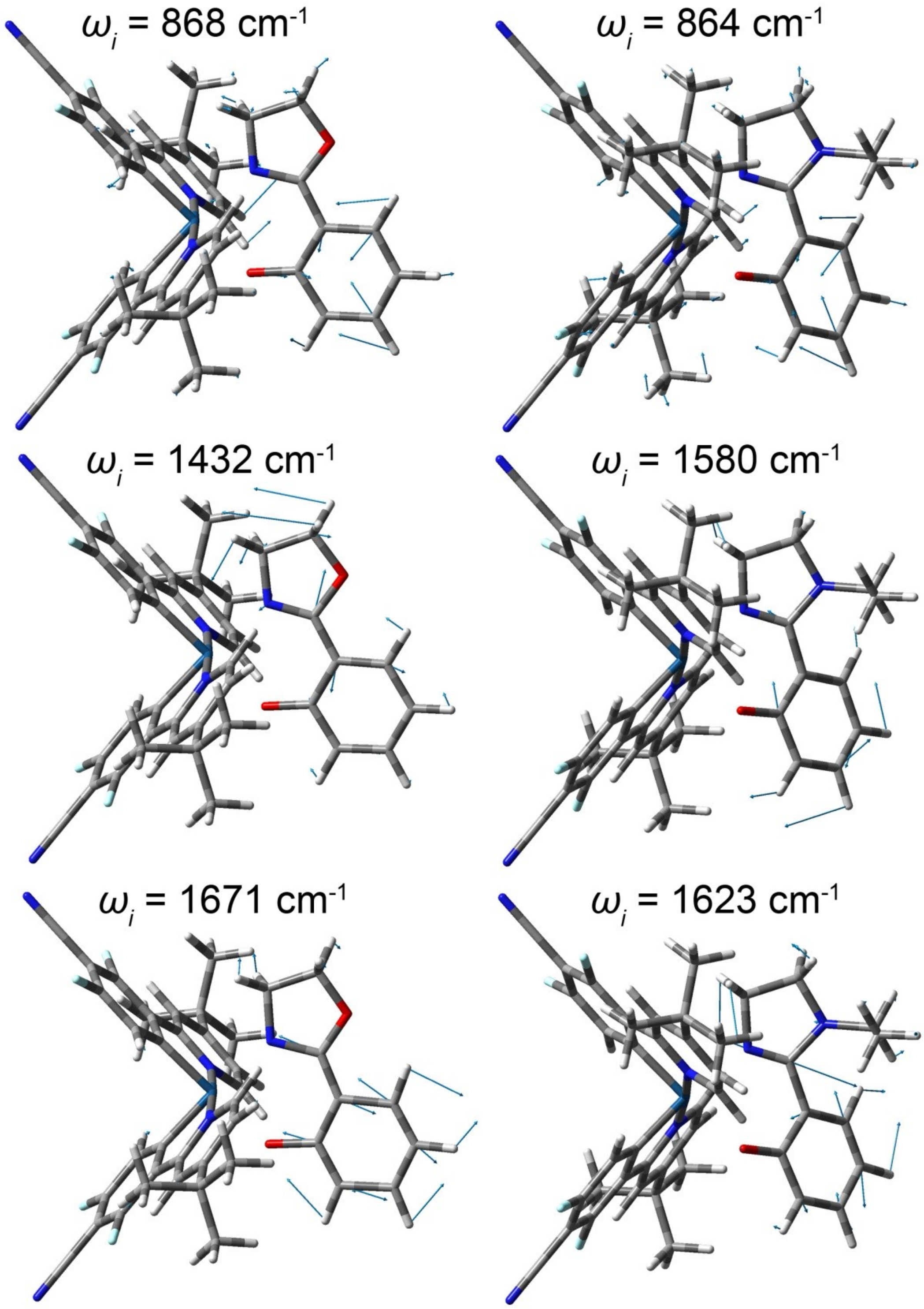
	State	λ	E	f	Configuration		Nature
1a	S_1	400	3.10	0.0087	H→L	(95%)	MLCT/LLCT
	S_3	360	3.44	0.0683	H-1→L	(93%)	MLCT/LC/LLCT
	S_5	344	3.61	0.0629	H→L+3	(92%)	MLCT/LC/LLCT
1b	S_1	407	3.05	0.0313	H→L	(91%)	MLCT/LLCT
	S_6	337	3.68	0.0570	H→L+3	(47%)	MLCT/LLCT
					H-2→L	(12%)	MLCT/LC/LLCT
	S_7	334	3.71	0.0516	H-2→L	(74%)	MLCT/LC/LLCT
2a	S_1	465	2.67	0.0054	H→L	(81%)	LLCT
	S_4	375	3.31	0.0348	H→L+3	(73%)	LLCT
	S_6	365	3.40	0.0331	H-1→L	(46%)	MLCT/LC/LLCT
					H→L+5	(36%)	LC/LLCT
2b	S_1	408	3.04	0.0092	H→L	(95%)	MLCT/LLCT
	S_5	345	3.60	0.0733	H-1→L	(50%)	MLCT/LLCT
					H-2→L	(33%)	MLCT/LC/LLCT
2c	S_1	472	2.63	0.0045	H→L	(88%)	LLCT
	S_3	396	3.13	0.0646	H→L+3	(90%)	LC/LLCT
	S_7	364	3.41	0.0650	H-1→L	(93%)	MLCT/LC/LLCT
2d	S_1	422	2.94	0.0158	H→L	(83%)	LLCT
	S_3	375	3.30	0.0488	H-1→L	(84%)	MLCT/LC/LLCT
	S_4	362	3.42	0.0485	H-1→L+1	(68%)	MLCT/LC/LLCT
3a	S_1	394	3.15	0.1334	H→L	(97%)	MLCT/LC
	S_4	354	3.50	0.0989	H-1→L+1	(65%)	MLCT/LC/LLCT
3b	S_1	457	2.72	0.0355	H→L	(99%)	MLCT/LC
	S_5	354	3.50	0.0640	H-1→L+1	(85%)	MLCT/LC/LLCT
	S_7	342	3.63	0.0796	H-2→L	(61%)	MLCT/LC/LLCT
3c	S_1	362	3.43	0.0464	H→L+1	(69%)	MLCT/LLCT
					H-1→L+1	(22%)	MLCT/LC/LLCT
	S_2	353	3.51	0.1741	H→L+2	(54%)	MLCT/LC/LLCT
					H→L	(30%)	MLCT/LC/LLCT
3d	S_1	437	2.84	0.0362	H→L	(96%)	MLCT/LC/LLCT
	S_3	378	3.28	0.0575	H→L+1	(90%)	MLCT/LC/LLCT

[a] "H" and "L" denote HOMO and LUMO respectively.

Table S7 Compositions (%) of major molecular orbitals[a] related to the transition from T_1 to S_0. Here L_A represents the ancillary ligand containing O and N1 atoms, C^N (I) and C^N (II) respectively refers to the phenylpyridine ligands containing C1 and N2 atoms, C2 and N3 atoms.

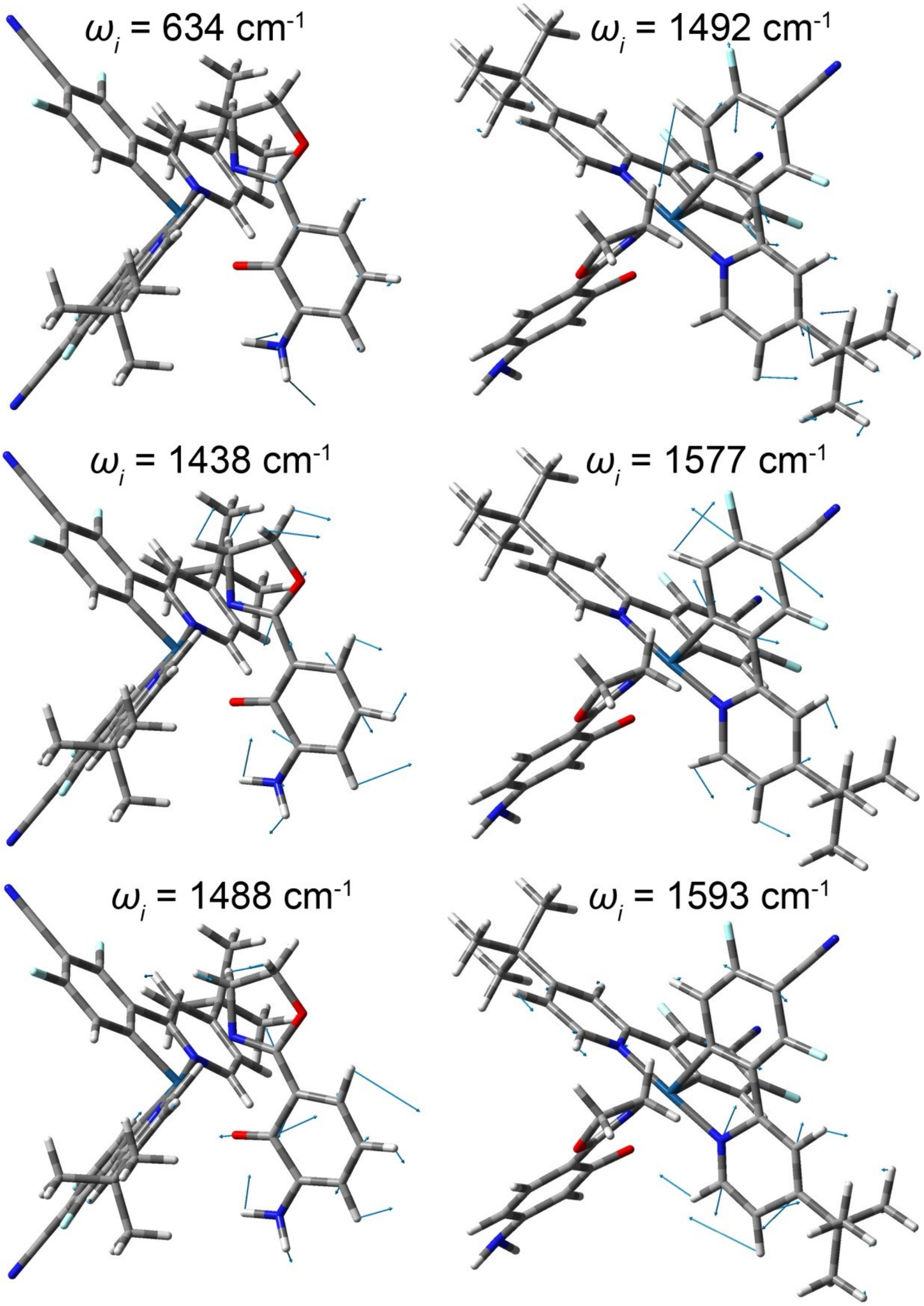
	Orbital	*E*(eV)	Composition(%)				Characteristics
			Ir(d)	L_A	C^N (I)	C^N (II)	
1a	L+2	-1.65	1.30	88.42	8.76	1.40	π*(L_A)
	H	-5.29	14.35	79.75	2.27	3.07	d(Ir)+π(L_A)
1b	L+2	-1.65	1.39	66.36	0.80	31.34	π*(L_A +C^N (II))
	L+1	-1.74	3.59	25.09	16.30	53.95	π*(L_A +C^N (II))
	H	-5.22	17.61	74.35	4.48	3.02	d(Ir)+π(L_A)
2a	L+2	-1.41	1.36	84.89	12.23	0.98	π*(L_A +C^N (I))
	H	-4.41	1.87	97.02	0.15	0.60	π(L_A)
2b	L	-2.12	3.07	0.96	2.78	92.28	π*(C^N (II))
	H	-5.14	13.96	79.43	2.21	3.86	d(Ir)+π(L_A)
	H-2	-5.71	26.03	36.24	17.59	19.67	d(Ir)+π(L_A +C^N(I)+C^N(II))
	H-3	-6.29	37.16	16.08	17.96	28.49	d(Ir)+π(L_A +C^N(I)+C^N(II))
2c	L+2	-1.47	1.21	94.61	3.71	0.33	π*(L_A)
	H	-4.37	3.12	95.44	0.34	0.64	d(Ir)+π(L_A)
2d	L+2	-1.41	1.29	89.71	7.73	0.89	π*(L_A)
	H	-4.82	3.49	95.19	0.23	0.71	d(Ir)+π(L_A)
3a	L	-2.43	0.31	99.07	0.26	0.12	π*(L_A)
	H	-5.80	17.27	77.14	2.80	2.21	d(Ir)+π(L_A)
3b	L	-2.92	0.76	98.98	0.16	0.08	π*(L_A)
	H	-5.74	16.26	78.71	2.17	2.30	d(Ir)+π(L_A)
3c	L+2	-2.02	2.62	19.70	67.68	9.06	π*(L_A +C^N (I))
	L+1	-2.11	1.01	26.89	4.11	67.42	π*(L_A +C^N (II))
	H	-5.90	24.67	54.62	5.06	15.16	d(Ir)+π(L_A +C^N (II))
3d	L	-3.16	0.31	86.08	0.50	13.01	π*(L_A +C^N (II))
	H	-5.71	23.24	52.29	7.25	16.75	d(Ir)+π(L_A +C^N (II))
	H-1	-6.05	30.57	25.07	23.62	20.35	d(Ir)+π(L_A +C^N(I)+C^N(II))

[a] "H" and "L" denote HOMO and LUMO respectively.



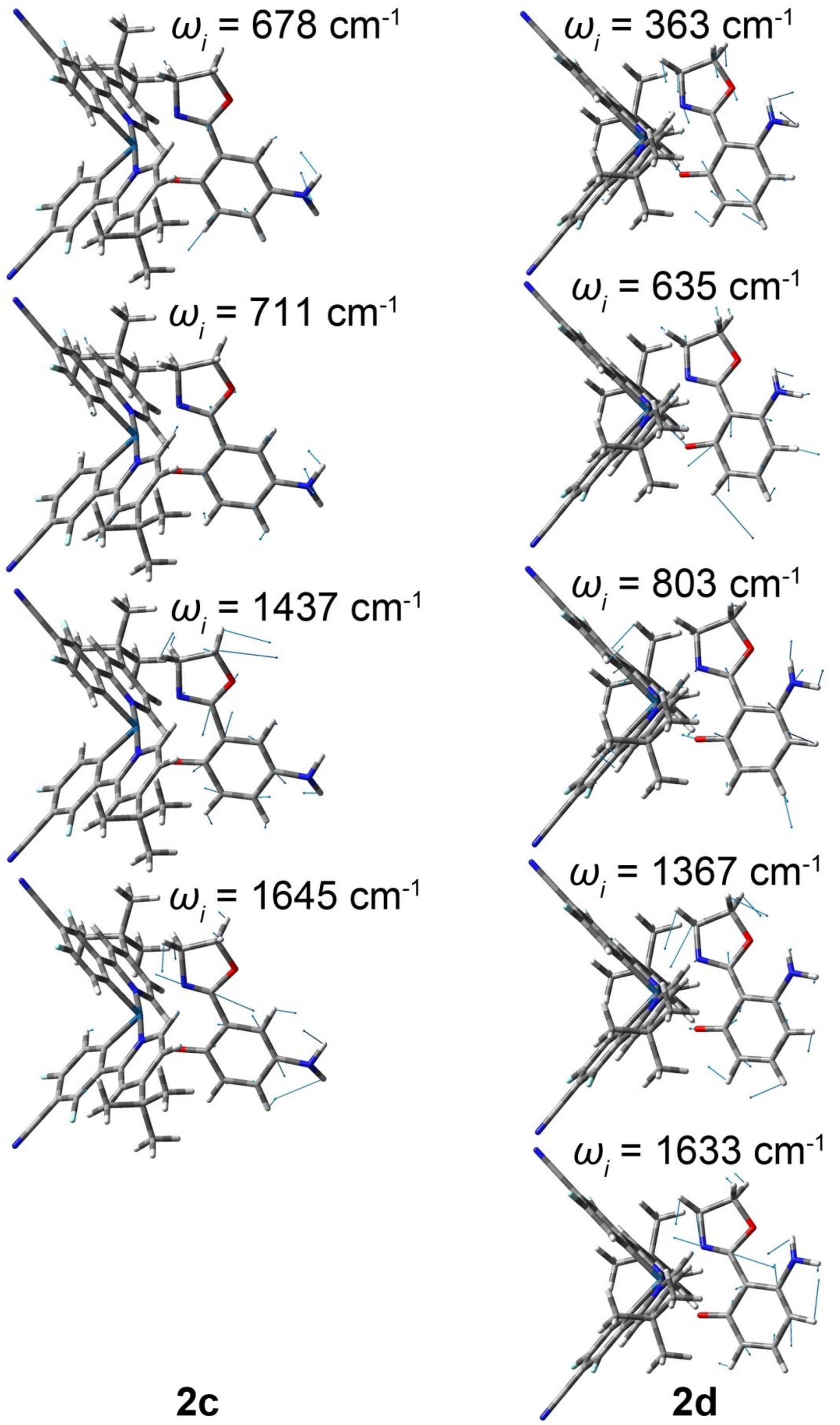
ω_i = 868 cm^{-1}
ω_i = 864 cm^{-1}
ω_i = 1432 cm^{-1}
ω_i = 1580 cm^{-1}
ω_i = 1671 cm^{-1}
ω_i = 1623 cm^{-1}

1a **1b**

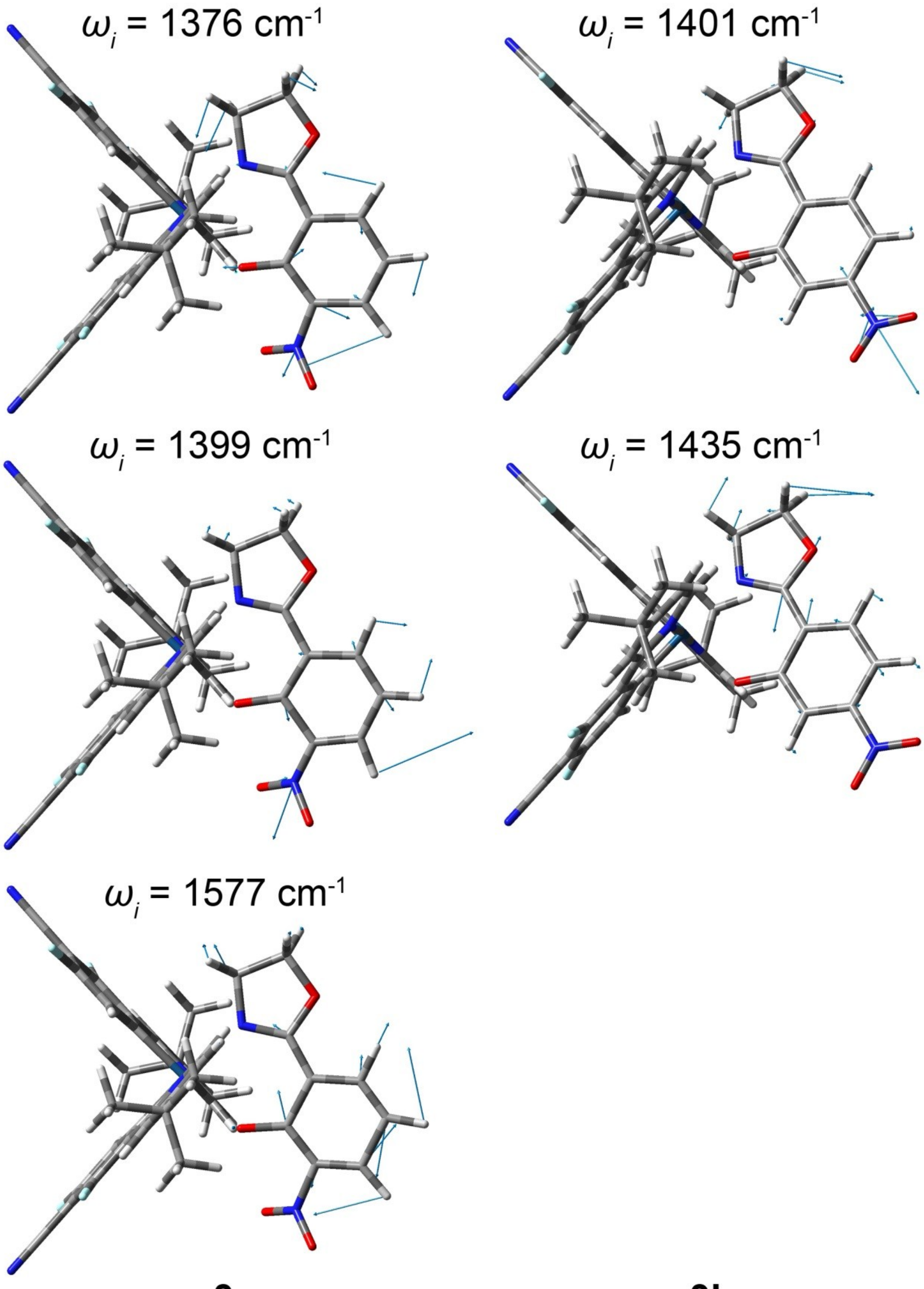


ω_i = 634 cm^{-1}
ω_i = 1492 cm^{-1}
ω_i = 1438 cm^{-1}
ω_i = 1577 cm^{-1}
ω_i = 1488 cm^{-1}
ω_i = 1593 cm^{-1}

2a **2b**



ω_i = 678 cm-1
ω_i = 711 cm-1
ω_i = 1437 cm-1
ω_i = 1645 cm-1
ω_i = 363 cm-1
ω_i = 635 cm-1
ω_i = 803 cm-1
ω_i = 1367 cm-1
ω_i = 1633 cm-1
2c
2d



ω_i = 1376 cm^{-1}
ω_i = 1401 cm^{-1}
ω_i = 1399 cm^{-1}
ω_i = 1435 cm^{-1}
ω_i = 1577 cm^{-1}

3a **3b**

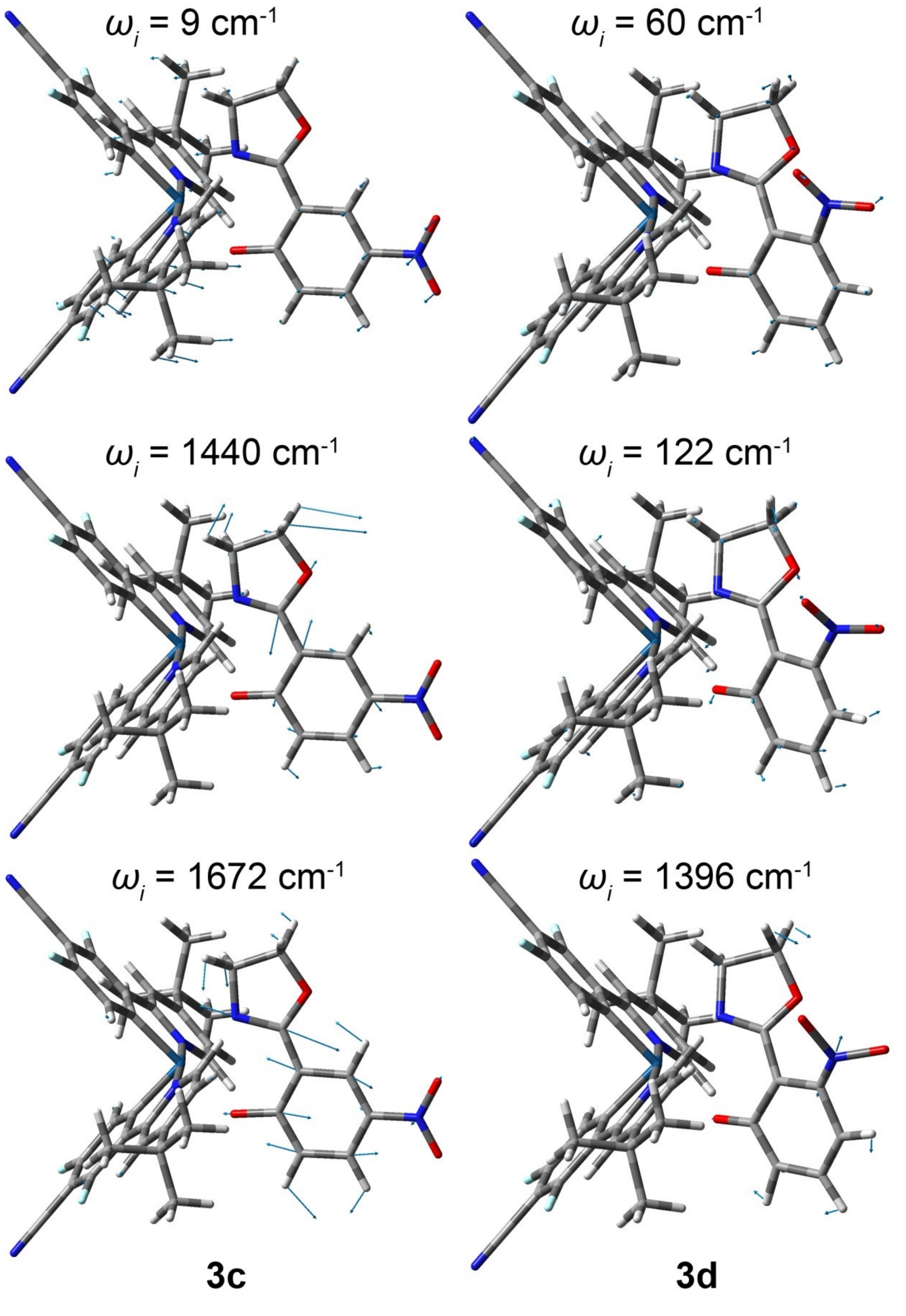


Figure S4. Schemes for the vibrational displacement vectors of the main normal modes with large vibration energy.

Table S8 Selected reorganization energies (λ_i/cm^{-1}) with the value larger than 5.0 cm^{-1} and the corresponding normal mode frequencies (ω_i/cm^{-1}) for studied complexes.

1a		**1b**		**2a**		**2b**		**2c**		**2d**	
ω_i	λ_i	ω_i	λ_i	ω_i	λ_i	ω_i	λ_i	ω_i	λ_i	ω_i	λ_i
16	11.9	15	58.0	19	20.2	12	5.0	12	11.4	15	21.6
18	9.6	16	23.3	37	6.2	16	42.8	42	14.4	22	9.0
20	40.4	27	45.4	62	65.3	18	12.5	77	14.6	29	11.4
24	5.2	31	15.9	112	85.4	20	50.7	103	27.8	37	10.6
42	89.4	44	6.2	118	9.6	28	18.1	119	40.1	38	74.3
47	10.3	60	147.9	231	5.4	38	5.5	185	6.3	64	13.1
89	5.1	78	7.3	261	6.6	46	36.6	197	6.8	113	52.0
118	78.5	94	11.9	267	9.3	69	23.0	213	18.3	124	21.1
121	85.8	108	42.9	324	8.5	78	10.0	266	5.1	128	12.1
128	6.1	144	10.0	329	5.2	83	6.0	282	5.2	132	6.2
134	7.9	149	33.1	341	120.8	131	12.0	296	8.9	134	7.4
142	7.0	157	8.3	370	17.4	154	24.8	367	9.0	141	6.2
147	10.7	174	13.7	404	178.9	158	5.9	372	100.0	147	6.5
168	18.7	182	26.3	449	33.1	249	6.4	427	68.4	150	13.1
203	6.1	187	30.4	494	29.0	320	14.3	467	16.5	186	7.1
210	14.6	190	97.4	504	5.2	409	8.7	502	61.8	230	5.9
241	7.9	207	8.2	508	5.3	415	12.0	508	54.1	259	23.5
369	87.0	218	13.5	512	84.4	485	17.9	509	166.9	315	63.1
414	7.6	225	7.6	515	25.3	486	14.8	514	10.5	322	17.9
422	33.0	226	6.7	579	11.8	493	6.3	554	34.3	363	231.2
540	8.6	257	8.9	623	127.2	502	6.3	678	750.6	444	41.1
573	62.2	273	5.6	634	788.1	505	10.5	693	21.6	488	12.0
613	14.0	279	11.6	659	17.6	551	6.0	695	80.4	546	8.6
615	31.5	289	7.9	712	7.3	607	6.5	699	7.8	574	16.0
669	9.8	309	45.3	717	21.2	669	28.2	709	22.6	635	142.3
669	6.4	358	5.9	728	13.4	710	32.6	711	429.6	646	5.1
865	16.2	369	69.3	848	133.3	712	7.3	713	128.9	698	11.6
868	151.8	422	51.1	895	59.8	934	11.4	733	22.2	700	7.2
869	15.4	495	15.6	995	8.0	1044	39.1	762	19.8	726	7.7
938	30.5	549	6.2	1056	6.1	1047	5.9	830	21.0	795	43.2
972	6.3	569	42.0	1058	10.4	1050	33.6	849	20.9	801	59.7
1019	9.2	601	74.2	1085	32.8	1056	44.6	872	81.7	803	137.1
1050	9.3	637	12.2	1132	10.6	1058	24.4	876	32.3	928	41.6
1064	11.5	834	5.9	1143	43.3	1071	46.9	880	7.6	1041	19.5
1100	12.8	864	112.1	1191	28.3	1151	22.5	884	16.0	1127	8.3
1133	6.8	865	19.1	1248	6.0	1151	7.9	885	122.7	1130	23.7
1269	32.0	877	7.2	1306	11.8	1165	5.9	1059	10.1	1132	9.7
1382	46.6	944	6.6	1322	28.4	1222	30.4	1097	12.0	1251	17.8
1402	59.8	965	6.0	1324	14.5	1237	23.7	1129	6.7	1333	6.7
1432	163.8	972	9.2	1325	12.0	1280	20.4	1134	16.5	1339	17.6

1490	29.8	1046	8.3	1382	38.0	1291	34.8	1262	26.4	1367	166.4
1507	56.1	1047	11.3	1418	38.5	1325	30.3	1268	18.3	1395	48.4
1578	83.7	1063	11.4	1438	414.9	1332	63.3	1319	6.8	1426	8.2
1646	138.5	1120	30.1	1458	7.3	1335	25.5	1380	20.3	1493	43.5
1649	15.1	1157	10.1	1488	280.5	1348	6.0	1400	95.8	1633	182.9
1664	6.5	1205	18.6	1501	47.3	1459	15.8	1437	396.2	1647	61.1
1671	236.1	1243	7.2	1539	5.2	1492	163.5	1477	9.3	1658	13.6
		1265	25.6	1592	71.5	1505	17.9	1512	21.4		
		1275	8.2	1594	5.8	1516	6.8	1517	9.0		
		1292	5.2	1632	84.5	1517	73.8	1582	48.6		
		1318	6.4	1646	67.2	1525	35.9	1645	158.3		
		1345	13.7	1649	5.8	1527	125.4	1649	12.0		
		1348	6.1	1656	7.7	1536	5.7	1657	9.8		
		1379	97.5	1663	17.5	1577	138.5	1694	29.1		
		1384	56.2	1667	159.9	1593	215.4	3546	31.7		
		1396	6.6	3559	32.7	1593	29.5				
		1457	66.6			1649	87.4				
		1484	34.6			1655	45.3				
		1503	37.6			1660	19.0				
		1506	22.0			1664	5.1				
		1507	20.2								
		1520	22.2								
		1548	8.1								
		1580	194.0								
		1623	258.5								
		1655	40.7								
		1660	68.6								
		1661	92.1								
		1664	28.4								

3a		**3b**		**3c**		**3d**			
ω_i	λ_i	ω_i	λ_i	ω_i	λ_i	ω_i	λ_i	ω_i	λ_i
12	25.2	44	5.9	9	295.1	15	18.0	1225	80.2
17	6.3	47	7.7	36	15.4	22	119.9	1251	8.5
27	41.3	85	16.6	88	12.0	26	39.0	1276	6.2
28	45.9	108	7.6	99	30.6	30	8.9	1317	23.0
31	8.8	121	8.1	106	35.9	36	142.6	1396	764.9
51	24.9	126	5.5	129	7.5	60	267.6	1431	154.6
63	10.2	208	7.8	140	5.5	82	10.8	1482	10.7
83	5.4	236	5.7	158	23.3	84	7.9	1567	110.6
109	25.6	262	20.2	176	36.0	92	73.0	1625	37.2
122	132.4	278	28.4	205	5.2	122	222.9	1655	26.2
124	14.6	486	5.2	271	9.4	126	26.8	1657	31.8
146	28.2	521	62.9	284	12.7	132	31.5	1680	21.2
181	42.5	599	102.0	330	14.2	134	5.6		

188	17.7	696	18.0	395	15.2	151	118.8
191	19.0	833	81.2	421	6.4	158	41.2
207	11.0	928	68.0	532	13.1	170	20.2
216	17.3	967	18.1	721	18.9	181	35.6
227	12.9	987	33.1	846	36.0	183	14.0
272	9.9	1089	62.6	867	10.7	188	18.6
273	8.2	1110	29.5	884	26.5	224	7.5
281	6.9	1177	17.2	886	133.9	270	7.8
313	31.2	1258	8.0	1018	9.0	349	83.7
330	32.2	1348	13.5	1055	17.9	352	21.8
430	127.0	1351	68.1	1130	5.3	389	20.6
444	15.9	1383	26.7	1152	10.3	409	6.7
532	8.9	1401	386.6	1153	22.9	410	6.3
557	53.3	1435	198.9	1247	7.0	469	120.8
613	17.6	1491	54.5	1264	22.3	514	10.0
615	91.4	1581	86.5	1328	7.5	516	125.6
730	11.6	1638	40.7	1379	69.3	610	12.6
743	11.8	1653	33.1	1384	7.4	640	110.3
822	10.5	1657	12.0	1395	25.5	646	5.8
857	213.5	1681	112.0	1440	236.5	691	27.7
861	5.2			1511	22.0	714	17.1
869	11.9			1570	40.9	729	9.5
893	29.4			1655	31.2	754	44.5
1148	47.6			1660	7.0	828	61.0
1190	21.2			1662	5.1	835	93.2
1230	31.8			1664	17.2	903	57.6
1324	9.9			1672	544.6	938	26.3
1376	233.4					966	19.7
1399	204.0					988	62.1
1431	30.8					991	6.1
1495	8.0					1050	7.4
1577	155.6					1125	14.7
1647	15.7					1181	6.5
1680	65.2					1220	58.2

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