Supplementary information data

Table 1S Energies of frontier molecular orbitals obtained from b3lyp/cep-4g wavefunction for sensitizers.

	N3			Deprotonated-**N3**		
		Energy (eV)			Energy (eV)	
MO[a]	Type[b]	In vacuo	In CH_3CN	Type[b]	In vacuo	In CH_3CN
118 (V)	bpy(π*)	-4.12	-3.87	bpy(π*)	5.58	-2.56
117 (V)	bpy(π*)	-4.32	-4.10	bpy(π*)	5.54	-2.58
116 (V)	bpy(π*)	-4.42	-4.18	bpy(π*)	5.43	-2.70
115 (V)	bpy(π*)	-4.70	-4.53	bpy(π*)	4.74	-3.37
114 (V)	bpy(π*)	-4.82	-4.61	bpy(π*)	4.67	-3.44
113 (O)	Ru(d*)	-6.03	-6.38	COO^-	2.90	-5.64
112 (O)	Ru(d*)	-6.15	-6.65	COO^-	2.90	-5.64
111 (O)	NCS	-6.25	-6.67	COO^-	2.90	-5.64
110 (O)	Ru(d*)	-6.33	-6.73	COO^-	2.90	-5.64
109 (O)	Ru(d*)	-7.63	-7.71	COO^-	2.85	-5.67

[a]O: occupied; V: virtual. Bold characters are used for the HOMO (**113**) and the LUMO (**114**).

[b]Dominant moiety contributing to molecular orbital.

Table 2S. Selected calculated excited states for **N3** in vacuo

State	E (eV)[a]	f[b]	$\phi_o \rightarrow \phi_v$[c]	Character[d]
8	1.1069	0.0317	112→115	MLCT1
14	1.4581	0.0306	113→117	MLCT1
			113→119	MLCT1
16	1.5029	0.0356	112→117	MLCT1
17	1.5164	0.0601	112→118	MLCT1
			113→117	MLCT1
18	1.5330	0.0390	110→117	MLCT1
29	2.4302	0.1079	107→114	MLCT1
32	2.6547	0.0275	113→121	MLCT1
33	2.7102	0.1578	109→116	MLCT1
37	2.8165	0.0708	108→117	MLCT1
44	2.9536	0.1266	109→118	MLCT1
52	3.0545	0.0207	109→119	MLCT1
54	3.1364	0.0368	107→118	MLCT1
64	3.3631	0.0733	107→119	MLCT1
66	3.6345	0.1002	111→124	MBCT
67	3.6459	0.0511	101→114	LBCT
69	3.6796	0.0204	113→126	MLCT1
74	3.7649	0.1052	101→115	LBCT
75	3.7689	0.2091	102→115	LBCT
80	3.8414	0.0518	112→127	MBCT

[a]Energy above the ground state (vertical excitation). [b]Oscillator strength. [c]Occupied (ϕ_o) to virtual (ϕ_v) orbital excitation. [d]Character of excited state: metal-to-ligand (dcbpy) charge transfer (MLCT1), metal-to-ligand (phen) charge transfer (MLCT2), metal-to-ligand (dppz) charge transfer (MLCT3), ligand-based charge transfer (LBCT, either intra- or inter-ligand charge transfer), or metal-based charge transfer (MBCT).

Table 3S. Selected calculated excited states for **N3** in CH_3CN

State	E (eV)	f	$\phi_o \rightarrow \phi_v$	Character
1	1.2288	0.0358	113→114	MLCT1
7	1.5826	0.0222	110→115	MLCT1
8	1.6797	0.0363	111→115	MLCT1
9	1.7363	0.0546	113→116	MLCT1
10	1.8667	0.0759	113→117	MLCT1
16	2.1033	0.0327	113→119	MLCT1
18	2.1509	0.0346	111→117	MLCT1
25	2.4316	0.0297	108→115	MLCT1
29	2.6275	0.1956	107→114	MLCT1
35	2.9789	0.1148	109→116	MLCT1
37	3.0367	0.1831	108→117	MLCT1
38	3.1083	0.0334	107→116	MLCT1
43	3.2418	0.0267	108→118	MLCT1
44	3.2603	0.0339	113→121	MLCT1
			109→118	MLCT1
46	3.3763	0.0243	108→119	MLCT1
			107→119	MLCT1
47	3.3945	0.0497	108→118	MLCT1
			107→119	MLCT1
54	3.5621	0.0454	107→119	MLCT1
67	3.7192	0.1990	112→124	MBCT
68	3.7287	0.2149	101→115	LBCT
69	3.7387	0.3887	102→115	LBCT
			112→124	MBCT

Table 4S. Selected calculated excited states for deprotonated **N3** in vacuo

State	E (eV)	f	$\phi_o \rightarrow \phi_v$	Character
5	1.2899	0.0049	113→114	LBCT
			112→115	LBCT
6	1.2912	0.0038	112→114	LBCT
			113→115	LBCT
7	1.3403	0.0112	107→114	LBCT
			106→115	LBCT
15	1.5307	0.0134	103→114	MLCT1
22	1.5894	0.0063	103→115	MLCT1
23	1.7333	0.0043	100→114	LBCT
29	1.8146	0.0349	99→115	LBCT
32	1.8494	0.0194	100→115	LBCT
34	1.8713	0.0039	102→115	LBCT
			105→114	MLCT1
35	1.9863	0.0067	98→114	MLCT1
36	2.0124	0.0029	113→116	LBCT
40	2.0802	0.0141	98→115	MLCT1
41	2.0862	0.0045	106→117	LBCT
			107→116	LBCT
57	2.3422	0.0124	103→116	MLCT1
62	2.4088	0.0032	103→117	MLCT1
71	2.4906	0.0235	103→118	MLCT1
72	2.5217	0.0117	100→116	LBCT
78	2.5965	0.0229	103→119	MLCT1
			100→117	LBCT
79	2.6211	0.0057	100→117	LBCT
80	2.6213	0.0080	99→117	LBCT

Table 5S. Selected calculated excited states for deprotonated **N3** in CH_3CN

State	E (eV)	f	$\phi_o \rightarrow \phi_v$	Character
3	1.6366	0.0169	105→114	MLCT1
			111→114	LBCT
5	1.6419	0.0125	105→114	MLCT1
			111→114	LBCT
			110→115	LBCT
6	1.6878	0.0097	105→115	MLCT1
			109→115	LBCT
9	1.7565	0.0083	106→115	LBCT
			105→114	MLCT1
17	1.9063	0.0140	112→115	LBCT
			113→114	LBCT
19	1.9308	0.0308	103→115	MLCT1
			110→115	LBCT
23	1.9454	0.0116	108→115	LBCT
			103→115	MLCT1
26	1.9888	0.0289	104→115	MLCT1
			103→114	MLCT1
36	2.2553	0.0162	98→115	MLCT1
43	2.4671	0.0224	105→116	MLCT1
			109→116	LBCT
46	2.5397	0.0119	105→117	MLCT1
47	2.5697	0.0405	105→118	MLCT1
56	2.6989	0.0376	105→119	MLCT1
			103→116	MLCT1
59	2.7352	0.0063	103→117	MLCT1
61	2.7462	0.0076	113→118	LBCT
			112→117	LBCT
63	2.7553	0.0072	112→119	LBCT
65	2.7709	0.0154	104→118	MLCT1
73	2.7997	0.0096	97→114	MLCT1
75	2.8161	0.0145	110→119	LBCT
			111→118	LBCT

Table 6S. Selected calculated excited states for **1** in vacuo

State	E (eV)	f	$\phi_o \rightarrow \phi_v$	Character
14	1.4112	0.0239	101→106	MLCT1
			99→105	MLCT1
15	1.4538	0.0372	101→106	MLCT1
17	1.5009	0.0898	100→105	MLCT1
29	2.4317	0.0184	98→107	MLCT2
32	2.6062	0.0245	95→103	MLCT2
35	2.7173	0.0543	96→105	MLCT1
			96→104	MLCT2
37	2.8083	0.0429	95→105	MLCT1
41	2.9435	0.0362	97→106	MLCT1
			101→110	MLCT1
			100→109	MLCT2
43	2.9771	0.0209	100→109	MLCT2
46	3.0004	0.0194	101→110	MLCT1
52	3.1951	0.0587	99→110	MLCT1
53	3.2126	0.0349	99→110	MLCT1
			95→106	MLCT1
57	3.6081	0.0178	96→107	MLCT2
			99→111	MBCT
58	3.6301	0.0217	101→112	MLCT1
			101→113	MLCT1
59	3.6451	0.0504	93→102	LBCT
			101→112	MLCT2
60	3.6590	0.0438	101→113	MLCT2
61	3.6815	0.0295	93→102	LBCT
			96→107	MLCT2
63	3.7354	0.1126	91→102	LBCT
69	3.8349	0.0172	93→103	LBCT
74	3.8956	0.0289	100→114	MBCT
			99→113	MLCT1
77	3.9491	0.0273	90→102	LBCT

M(NCS) → dcbpy = MLCT1; M(NCS) → phen = MLCT2; NCS → NCS = MBCT

Table 7S. Selected calculated excited states for **1** in CH_3CN

State	E (eV)	f	$\phi_o \rightarrow \phi_v$	Character
1	1.2187	0.0274	101→102	MLCT1
5	1.6672	0.0250	99→102	MLCT1
7	1.7980	0.0696	101→105	MLCT1
13	2.0319	0.0313	99→103	MLCT1
17	2.1683	0.0405	99→105	MLCT1
23	2.6457	0.0888	95→102	MLCT1
25	2.7972	0.0275	96→103	MLCT2
			96→105	MLCT1
31	2.9551	0.2201	96→103	MLCT2
33	3.0165	0.0429	95→103	MLCT2
			95→105	MLCT1
39	3.2152	0.0252	96→106	MLCT1
			98→107	MLCT2
43	3.3865	0.0485	95→106	MLCT1
46	3.4914	0.0320	94→102	LBCT
52	3.6897	0.0446	91→102	LBCT
			90→102	LBCT
54	3.7272	0.0644	92→102	LBCT
55	3.7295	0.1824	90→102	LBCT
			91→102	LBCT
56	3.7329	0.0667	100→111	MBCT
57	3.7563	0.0461	100→110	MLCT1
65	3.9500	0.0317	94→103	LBCT
			94→105	LBCT
69	4.0633	0.0276	96→107	MLCT2
77	4.1509	0.0317	90→103	LBCT

M(NCS) → dcbpy = MLCT1; M(NCS) → phen = MLCT2

Table 8S. Selected calculated excited states for deprotonated **1** in vacuo

State	E (eV)	f	$\phi_o \rightarrow \phi_v$	Character
17	0.9661	0.0076	101→104	LBCT
19	0.9858	0.0058	100→104	LBCT
20	1.0242	0.0090	92→102	MLCT2
28	1.3088	0.0221	92→103	MLCT2
30	1.3783	0.0630	93→103	MLCT2
39	1.8532	0.0062	95→104	MLCT1
45	1.9895	0.0167	94→104	MLCT1
50	2.0638	0.0057	91→102	MLCT2
			95→105	MLCT2
			90→102	MLCT2
52	2.1322	0.0102	90→102	MLCT2
55	2.2113	0.0062	90→103	MLCT2
			94→105	MLCT2
			89→103	MLCT2
56	2.2311	0.0149	92→104	MLCT1
			93→104	MLCT1
58	2.2651	0.0050	92→105	MLCT2
			89→102	MLCT2
62	2.3406	0.0116	92→105	MLCT2
64	2.6073	0.0953	89→103	MLCT2
65	2.7226	0.0249	95→106	MLCT2
			95→107	MLCT1
67	2.7632	0.0459	95→107	MLCT1
			95→106	MLCT2
68	2.7672	0.0061	101→109	LBCT
			100→109	LBCT
72	2.8231	0.0060	94→106	MLCT2
			95→108	MLCT1
73	2.8419	0.0142	94→107	MLCT1
			95→108	MLCT1
75	2.8674	0.0102	88→102	LBCT

M(NCS) → dcbpy = MLCT1; M(NCS) → phen = MLCT2

Table 9S. Selected calculated excited states for deprotonated **1** in CH_3CN

State	E (eV)	f	$\phi_o \rightarrow \phi_v$	Character
4	1.5756	0.0259	97→102	LBCT
			97→103	LBCT
21	1.8391	0.0355	93→103	MLCT2
			95→102	MLCT2
22	1.8447	0.0119	95→102	MLCT2
27	1.9741	0.0269	94→104	MLCT1
			92→102	MLCT2
28	2.0223	0.0177	92→103	MLCT2
			92→102	MLCT2
			93→104	MLCT1
29	2.0734	0.0259	93→104	MLCT1
32	2.2884	0.0153	92→104	MLCT1
40	2.6233	0.0123	100→105	LBCT
			97→106	LBCT
			100→106	LBCT
41	2.6346	0.0258	97→106	LBCT
			100→105	LBCT
47	2.7539	0.0281	97→107	LBCT
50	2.8165	0.0142	90→102	MLCT2
53	2.8371	0.0510	94→106	MLCT2
55	2.8521	0.0245	93→105	MLCT2
58	2.9040	0.0473	90→103	MLCT2
			89→102	MLCT2
60	2.9282	0.0112	94→107	MLCT1
62	2.9979	0.0906	89→104	MLCT1
			90→104	MLCT1
63	3.0223	0.0113	93→107	MLCT1
69	3.2246	0.0311	92→107	MLCT1
			89→104	MLCT1
70	3.3756	0.0502	97→108	LBCT
80	3.6249	0.0123	88→103	LBCT

M(NCS) → dcbpy = MLCT1; M(NCS) → phen = MLCT2

Table 10S. Selected calculated excited states for **2** in vacuo

State	E (eV)	f	$\phi_o \rightarrow \phi_v$	Character
7	0.9850	0.0159	118→121	MLCT1
18	1.4134	0.0158	117→124	MLCT1
			119→125	MLCT1
19	1.4632	0.0402	119→125	MLCT1
21	1.5048	0.0824	118→124	MLCT1
28	2.1844	0.0196	114→120	MLCT3
30	2.2470	0.0331	113→120	MLCT3
34	2.4275	0.0362	113→121	MLCT1
			115→124	MLCT1
43	2.6948	0.0616	113→122	MLCT3
			116→127	MLCT3
44	2.7143	0.0374	114→124	MLCT1
46	2.7668	0.1574	113→123	MLCT3
47	2.8134	0.0410	118→128	MLCT1
			113→124	MLCT1
48	2.8325	0.0235	118→128	MLCT1
50	2.8714	0.0266	117→128	MLCT1
52	2.9515	0.0461	115→125	MLCT1
57	3.0038	0.0219	119→130	MLCT1
			119→131	MLCT3
58	3.0410	0.0198	114→125	MLCT1
61	3.1215	0.0208	112→120	LBCT
			113→125	MLCT1
			114→125	MLCT1
66	3.1896	0.0187	117→131	MLCT3
68	3.2311	0.0670	113→125	MLCT1
80	3.6304	0.1051	117→132	MBCT

M(NCS) → dcbpy = MLCT1; M(NCS) → dppz = MLCT3

Table 11S. Selected calculated excited states for **2** in CH_3CN

State	E (eV)	f	$\phi_o \rightarrow \phi_v$	Character
9	1.6356	0.0493	119→122	MLCT1
11	1.7913	0.0672	119→124	MLCT1
19	2.0341	0.0409	119→125	MLCT1
21	2.1350	0.0345	117→124	MLCT1
28	2.4374	0.0453	114→120	MLCT1
29	2.5296	0.056	113→120	MLCT3
30	2.6749	0.0762	113→121	MLCT1
35	2.8769	0.0334	115→123	MLCT3
40	2.9700	0.1501	119→127	MLCT3
41	2.9936	0.1022	119→127	MLCT3
42	2.9973	0.0559	112→120	LBCT
			119→127	MLCT3
			113→123	MLCT3
43	3.0413	0.0537	112→120	LBCT
			113→122	MLCT3
58	3.4500	0.0696	113→125	MLCT1
74	3.7101	0.1908	118→132	LMCT3
75	3.7185	0.3252	109→121	LBCT
76	3.7608	0.2458	112→124	LBCT
			112→122	LBCT
77	3.7844	0.1077	112→124	LBCT
			108→121	LBCT
			116→132	MBCT
78	3.8001	0.0479	108→121	LBCT
79	3.8436	0.4554	118→130	MLCT1
80	3.8508	0.1218	118→130	MLCT1

M(NCS) → dcbpy = MLCT1; M(NCS) → dppz = MLCT3; dppz → (NCS)M = LMCT3

Table 12S. Selected calculated excited states for deprotonated **2** in vacuo

State	E (eV)	f	$\phi_o \rightarrow \phi_v$	Character
5	0.3768	0.0188	116→120	MLCT3
15	0.9154	0.0070	116→121	MLCT3
			116→122	MLCT3
18	1.0906	0.0117	114→121	MLCT3
			116→122	MLCT3
			112→122	MLCT3
24	1.3561	0.0470	113→122	MLCT3
26	1.4342	0.0453	112→122	MLCT3
			113→122	MLCT3
30	1.5677	0.0214	118→123	LBCT
31	1.6249	0.0126	110→120	MLCT3
33	1.7567	0.0139	109→120	MLCT3
			108→120	MLCT3
36	1.8381	0.0399	118→124	LBCT
			119→124	LBCT
37	1.8445	0.0118	116→123	MLCT1
41	1.9706	0.0123	114→123	MLCT1
43	2.0585	0.0184	116→124	MLCT3
49	2.1870	0.0110	113→123	MLCT1
			112→123	MLCT1
50	2.1910	0.0131	110→122	MLCT3
			113→123	MLCT1
53	2.2201	0.0137	116→125	MLCT3
70	2.5442	0.0256	116→126	MLCT3
73	2.6724	0.0362	116→127	MLCT3
75	2.7279	0.2474	108→122	MLCT3
			118→128	LBCT
76	2.7535	0.0420	118→129	LBCT
80	2.8127	0.0105	112→126	MLCT3
			113→126	MLCT3

Table 13S. Selected calculated excited states for deprotonated **2** in CH_3CN

State	E (eV)	f	$\phi_o \rightarrow \phi_v$	Character
4	0.8903	0.0172	116→120	MLCT3
17	1.5083	0.0409	116→121	MLCT3
			116→122	MLCT3
24	1.7222	0.0427	119→123	LBCT
25	1.7711	0.0571	113→122	MLCT3
29	1.9235	0.0303	116→123	MLCT1
30	1.9448	0.0239	112→122	MLCT3
			112→121	MLCT3
35	2.1366	0.0202	114→123	MLCT1
36	2.1968	0.0293	109→120	MLCT3
43	2.4249	0.0158	112→123	MLCT1
46	2.6093	0.0342	116→124	MLCT3
			110→122	MLCT3
52	2.7278	0.0156	116→125	MLCT3
56	2.7798	0.0311	109→121	MLCT3
			108→121	MLCT3
61	2.8884	0.4117	119→127	LBCT
65	2.9503	0.0177	114→125	MLCT3
67	2.9698	0.0216	116→127	MLCT3
			113→125	MLCT3
68	2.9763	0.0171	116→127	MLCT3
			113→125	MLCT3
69	2.9977	0.0359	106→120	LBCT
70	3.0155	0.0142	113→126	MLCT3
74	3.0795	0.0422	113→126	MLCT3
75	3.0983	0.0374	110→123	MLCT1