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ARTICLE TYPE

Cite this: DOI: 00.0000/xxxxxxxxxx

Non-Linear Optical Properties of 2,7-Naphthyridine Derivatives for Optical Switching Application: A DFT Study†

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1 Supplementary information†

1.1 Structural details of studied compounds

2,7 naphthyridine, a donor moiety which is the parent compound and labelled as N. Then ten naphthyridine based structures are designed by using ethenyl bridge and nitrophenyl and triazine acceptors in the D-π-A chromophore format and are labelled as N1-N10. The IUPAC name of the designed compounds are given below. N=2,7 Naphthyridine N1=4-[(E)-2-phenyl ethenyl]-2,7 naphthyridine N2=4-[(E)-2-(4-nitrophenyl) ethenyl]-2,7 naphthyridine N3=4-[(E)-2-(3,5-dinitrophenyl) ethenyl]-2,7 naphthyridine N4=4-[(E)-2-(2,4,6-trinitrophenyl) ethenyl]-2,7 naphthyridine N5=4-[(E)-2-(4-phenylphenyl) ethenyl]-2,7 naphthyridine N6=4-[(E)-2-[4-(2,4,6-trinitrophenyl) phenyl] ethenyl]-2,7 naphthyridine N7=4-[(E)-2-(4-[3,5-bis(4-nitrophenyl)-1,3,5-triazin-2-yl] phenyl) ethenyl]-2,7 naphthyridine N8=4-[(E)-2-4-[3,5-bis(4-nitrophenyl) phenyl] phenyl ethenyl]-2,7 naphthyridine N9=4-[(E)-2-[4-(4-nitrophenyl)-2,5-dipropoxy phenyl] ethenyl]-2,7 naphthyridine N10= 4-[(E)-2-[2,5-bis(tert-butoxy)-4-[(E)-2-(3,5-dinitrophenyl) ethenyl] phenyl] ethenyl]-2,7 naphthyridine.

1.2 Optimised geometry of studied compounds

The optimised geometry of parent compound N and designed compounds N1-N10 computed using DFT-B3LYP/6-311G(d p) level of theory are shown in Fig. 1.

1.3 Comparison of theoretical and experimental bond length and bond angle

A comparison of theoretical and experimental values of selected bond length (Å) and bond angle (degree) of studied compounds N and N1-N10 are given in Table 1 and Table 2 respectively.

1.4 Polarization scan of HRS intensity

A polar graph is plotted between the normalized HRS intensity and polarisation angle ψ for parent compound N and designed compounds N1-N10 in gas phase for dynamic case (1064 nm and 1907 nm) are shown in Fig. 2.

1.5 HRS hyperpolarizability and depolarization ratio of studied compounds

The Static and Dynamic HRS hyperpolarizability (β_{HRS} $\times 10^{-30}$ esu) and Depolarization Ratio (DR) for parent compound N and designed compounds N1-N10 computed at DFT-B3LYP/6-311G(d p) level of theory in gas phase are given in Table 3.

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† Electronic Supplementary Information (ESI) available: Structural details of studied compounds, Optimised geometry of parent compound N and designed compounds N1-N10, Theoretical and experimental values of selected bond length (Å) of parent compound N and designed compounds N1-N10, Theoretical and experimental values of selected bond angle (degree) of parent compound N and designed compounds N1-N10, Polar representation of HRS intensity in atomic unit (a.u.) as a function of polarization angle ψ for dynamic case (a) 1064 nm for compounds N1-N10 (b)1907 nm for compounds N and N1-N10 in gas phase, Static and Dynamic HRS hyperpolarizability (β_{HRS} $\times 10^{-30}$ esu) and Depolarization Ratio (DR) for parent compound N and designed compounds N1-N10 computed at DFT-B3LYP/6-311G(d p) level in gas phase.

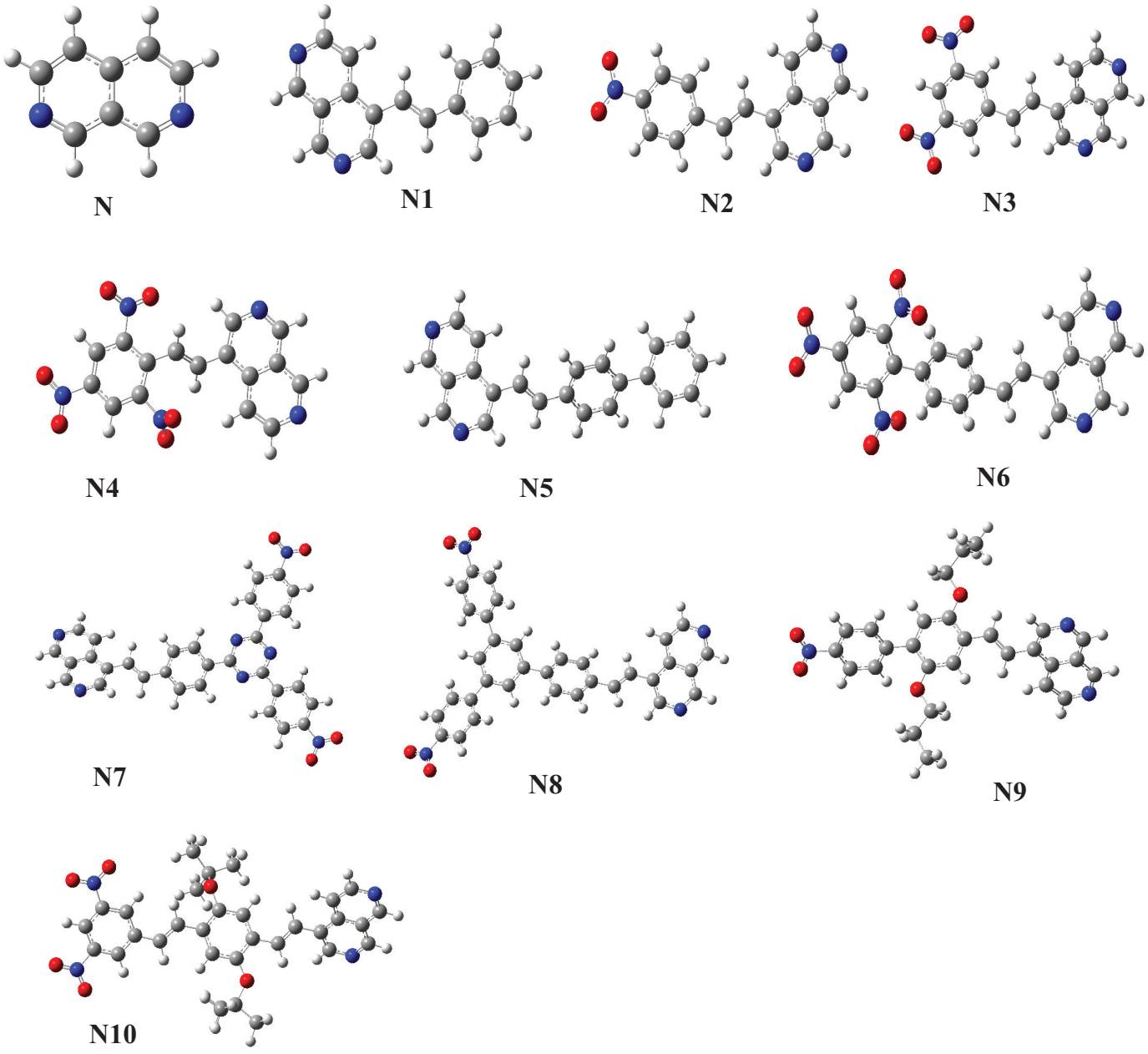

Fig. 1 Optimised geometry of parent compound N and designed compounds N1-N10.

Table 1 Theoretical and experimental values of selected bond length (Å) of parent compound N and designed compounds N1-N10

Bond length	N	N1	N2	N3	N4	N5	N6	N7	N8	N9	N10	Experimental value
C1-C2	1.3733	1.3742	1.3877	1.3874	1.3868	1.3879	1.3874	1.3879	1.3877	1.3884	1.3886	1.3683
C1-N16	1.3617	1.3600	1.3536	1.3533	1.3537	1.3542	1.3542	1.3536	1.3540	1.354	1.3538	1.3552
C5-N16	1.3136	1.3132	1.3144	1.3145	1.3146	1.3143	1.3143	1.3145	1.3144	1.3145	1.3147	1.3051
C4-C5	1.4183	1.4186	1.4162	1.4161	1.4164	1.4162	1.4163	1.4161	1.4162	1.4161	1.4159	1.4111
C3-C4	1.4212	1.4215	1.4214	1.4214	1.4209	1.4215	1.4212	1.4215	1.4214	1.4216	1.4217	1.4073
C2-C3	1.4160	1.4168	1.4327	1.4328	1.4322	1.4303	1.4325	1.4330	1.4329	1.4331	1.4334	1.4206
C3-C9	1.4160	1.4326	1.4164	1.4162	1.4160	1.4169	1.4165	1.4168	1.4168	1.4169	1.4169	1.3993
C9-C12	1.3733	1.3877	1.3746	1.3747	1.3751	1.3742	1.3744	1.3748	1.3743	1.3742	1.3743	1.3513
C12-N15	1.3617	1.3545	1.3597	1.3595	1.3596	1.3600	1.3597	1.3597	1.3598	1.3600	1.3600	1.3532
N15-C10	1.3136	1.3142	1.3130	1.3129	1.3129	1.3132	1.3132	1.3130	1.3131	1.3132	1.3131	1.3234
C4-C10	1.4183	1.4162	1.4186	1.4187	1.4185	1.4186	1.4187	1.4188	1.4187	1.4187	1.4187	1.4264
C5-H11	1.0887	1.0886	1.0881	1.0880	1.0881	1.0882	1.0881	1.0881	1.0881	1.0882	1.0881	0.9299
C1-H7	1.0854	1.0855	1.0852	1.0854	1.0853	1.0852	1.0853	1.0853	1.0852	1.0852	1.0851	0.9311
C9-H6	1.0841	1.0823	1.0823	1.0823	1.0827	1.0822	1.0823	1.0822	1.0822	1.0822	1.0822	0.9290
C12-H14	1.0854	1.0853	1.0854	1.0853	1.0851	1.0855	1.0854	1.0854	1.0854	1.0855	1.0854	0.9298
C10-H13	1.0887	1.0882	1.0885	1.0884	1.0884	1.0886	1.0885	1.0885	1.0885	1.0886	1.0886	0.9299
C14-C16	–	1.3451	1.3458	1.3446	1.3429	1.3460	1.3452	1.3463	1.3457	1.3470	1.3475	1.3204
C16-H17	–	1.0831	1.0866	1.0860	1.0819	1.0873	1.0868	1.0868	1.0871	1.0835	1.0831	0.9300
C14-H15	–	1.0858	1.0858	1.0860	1.0860	1.0857	1.0859	1.0855	1.0857	1.0858	1.0857	0.9300
C16-C18	–	1.4657	1.4637	1.4656	1.4668	1.4632	1.4645	1.4626	1.4637	1.4612	1.4610	1.4567
C18-C20	–	1.4060	1.4081	1.4047	1.4108	1.4060	1.4058	1.4078	1.4060	1.4031	1.3993	1.3988
C20-C22	–	1.3885	1.3848	1.3854	1.3821	1.3855	1.3847	1.3832	1.3856	1.3912	1.3897	1.3767
C22-C24	–	1.3957	1.3929	1.3887	1.3871	1.4054	1.400	1.4044	1.4048	1.4124	1.4125	1.3995
C24-C21	–	1.3925	1.3899	1.3859	1.3832	1.4016	1.3971	1.4010	1.4011	1.4006	1.4069	1.3777
C21-C19	–	1.3909	1.3871	1.3879	1.3871	1.3882	1.3871	1.3859	1.3882	1.3934	1.3895	1.3792
C19-C18	–	1.4045	1.4067	1.4034	1.4130	1.4042	1.4042	1.4062	1.4042	1.4126	1.4243	1.4016
C21-H25	–	1.0841	1.0809	–	1.0800	1.0839	1.0841	1.0814	1.0840	1.0807	1.0773	0.9299
C20-H23	–	1.0838	1.0828	1.0806	–	1.0838	1.083	1.0833	1.0836	1.0803	1.0809	0.9304
C19-029	–	–	–	–	–	–	–	–	–	1.3643	1.3614	1.3536

Table 2 Theoretical and experimental values of selected bond angle (degree) of parent compound N and designed compounds N1-N10

Bond angle	N	N1	N2	N3	N4	N5	N6	N7	N8	N9	N10	Experimental value
(C5,N16,C1)	117.36	117.02	117.57	117.55	117.54	117.64	117.60	117.60	117.63	117.65	117.62	118.10
(N16,C1,C2)	124.30	124.41	125.47	125.42	125.10	125.54	125.44	125.49	125.51	125.55	125.58	124.95
(C1,C2,C3)	118.95	119.32	117.03	117.14	117.59	116.82	117.02	116.96	116.90	116.80	116.79	117.20
(C2,C3,C4)	117.19	116.57	117.60	117.51	117.28	117.78	117.67	117.65	117.73	117.78	117.76	118.05
(C3,C4,C5)	118.25	118.54	118.80	118.81	118.77	118.77	118.76	118.79	118.77	118.78	118.80	117.68
(C4,C5,N16)	123.91	124.10	123.47	123.51	123.68	123.38	123.47	123.45	123.41	123.38	123.38	123.49
(C5,N16,C1)	117.36	117.36	117.57	117.55	117.54	117.64	117.60	117.60	117.63	117.65	117.62	118.10
(C3,C9,C12)	118.95	116.86	119.27	119.24	119.01	119.33	119.26	119.29	119.31	119.35	119.34	119.93
(C9,C12,N15)	124.30	125.53	124.42	124.42	124.50	124.41	124.41	124.42	124.41	124.41	124.42	123.88
(C12,N15,C10)	117.36	117.63	117.07	117.09	117.15	117.01	117.07	117.05	117.04	117.00	117.00	118.38
(N15,C10,C4)	123.91	123.39	124.04	124.01	123.93	124.11	124.05	124.05	124.08	124.11	124.10	121.45
(C10,C4,C3)	118.25	118.77	118.57	118.58	118.52	118.55	118.54	118.58	118.56	118.57	118.58	119.10
(C4,C3,C9)	117.19	117.77	116.60	116.62	116.85	116.56	116.64	116.57	116.57	116.52	116.52	116.88
(N16,C1,H7)	115.20	115.28	115.02	114.99	115.20	115.01	115.06	115.00	115.00	115.04	115.01	117.47
(H7,C1,C2)	120.48	120.48	119.47	119.55	119.65	119.42	119.46	119.47	119.46	119.38	119.38	119.58
(H6,C9,C12)	120.60	121.01	121.15	121.25	121.52	121.03	121.09	121.14	121.08	121.03	121.09	120.00
(H6,C9,C3)	120.44	119.65	119.56	119.49	119.44	119.63	119.63	119.55	119.59	119.59	119.55	120.06
(H14,C12,C9)	120.48	119.39	120.28	120.26	120.17	120.30	120.29	120.28	120.30	120.30	120.28	118.08
(H14,C12,N15)	115.20	115.05	115.28	115.30	115.32	115.28	115.29	115.28	115.28	115.27	115.28	115.05
(H11,C5,N16)	116.89	116.89	117.07	117.04	116.96	117.12	117.07	117.07	117.09	117.13	117.12	118.26
(H11,C5,C4)	119.19	118.99	119.45	119.44	119.35	119.49	119.45	119.46	119.48	119.48	119.48	118.25
(C14,C16,C18)	–	126.91	126.56	126.21	123.89	126.99	126.40	126.62	126.83	126.28	126.15	125.52
(C18,C19,C21)	–	121.21	121.45	120.18	123.56	121.51	121.40	121.41	121.49	119.75	119.32	121.83
(C19,C21,C24)	–	120.06	118.67	122.68	118.55	121.05	120.24	120.43	120.98	122.17	122.18	120.10
(C21,C24,C22)	–	119.50	121.64	119.28	121.44	117.53	118.98	118.60	117.68	118.16	118.38	119.21
(C24,C22,C20)	–	120.41	119.02	122.95	117.97	121.41	120.56	120.76	121.31	119.61	119.39	120.72
(C22,C20,C18)	–	120.86	121.11	119.93	124.29	121.14	121.08	121.09	121.15	122.36	122.58	121.08
(C19,C21,H25)	–	119.79	121.83	–	120.56	119.36	119.62	120.51	119.28	119.90	119.71	119.90
(H25,C21,C24)	–	120.14	119.48	–	120.87	119.56	120.12	119.05	119.70	119.88	118.06	120.00
(H23,C20,C18)	–	119.91	120.09	121.86	–	120.00	120.08	120.00	120.01	118.14	119.30	119.46

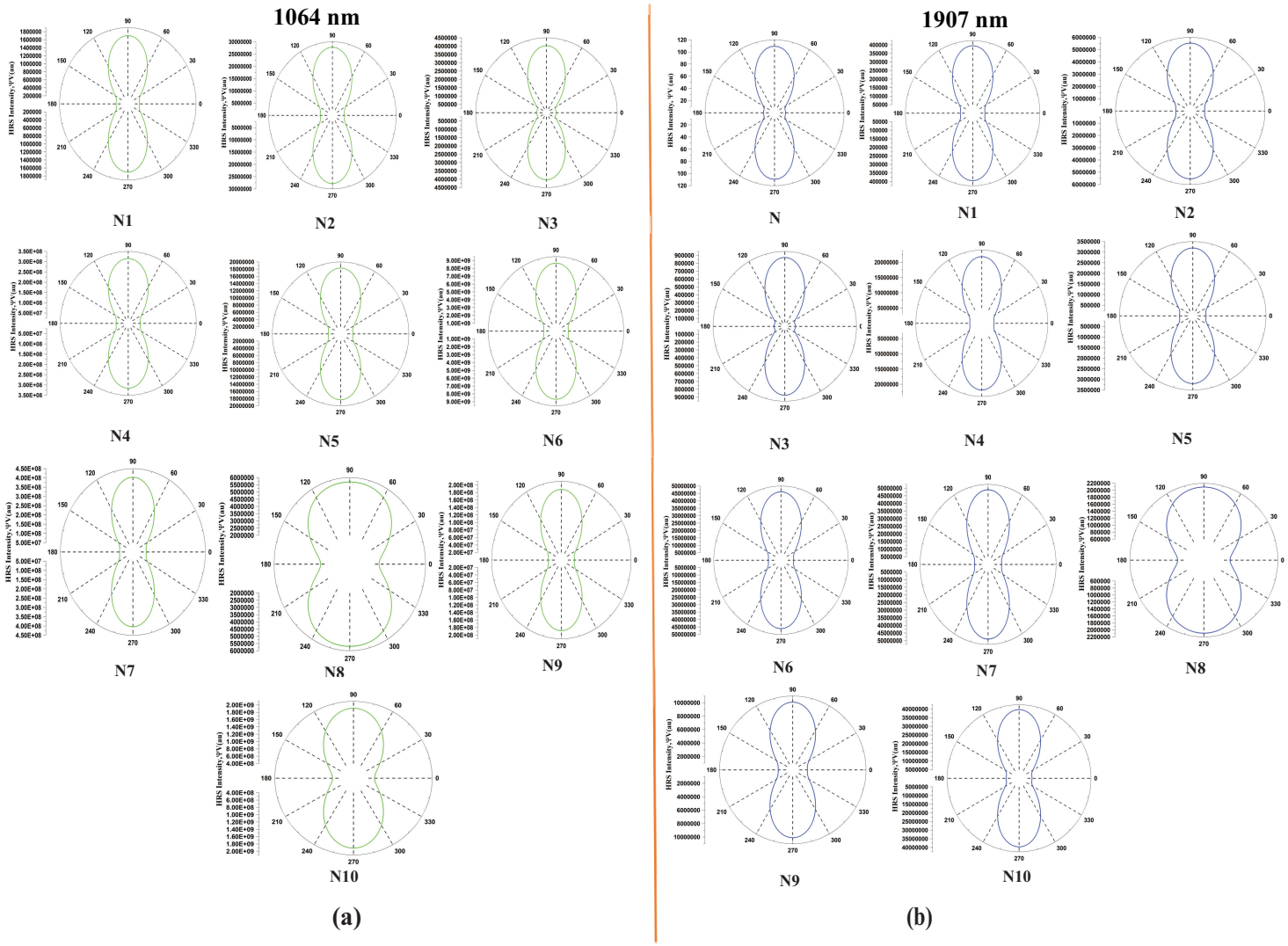

Fig. 2 Polar representation of HRS intensity in atomic unit (a.u.) as a function of polarization angle ψ for dynamic case (a) 1064 nm for compounds N1-N10 (b) 1907 nm for compounds N and N1-N10 in gas phase.

Table 3 Static and Dynamic HRS hyperpolarizability (β_{HRS} $\times 10^{-30}$ esu) and Depolarization Ratio (DR) for parent compound N and designed compounds N1-N10 computed at DFT-B3LYP/6-311G(d p) level in gas phase

Compound	$\beta_{HRS}{}^{a}$	DR^{a}	$\beta_{HRS}{}^{b}$	DR^{b}	$\beta_{HRS}{}^{c}$	DR^{c}
N	0.09	7.61	0.08	1.46	0.09	5.69
N1	4.58	4.97	12.31	5.21	5.94	5.06
N2	16.95	4.70	49.99	4.88	22.36	4.76
N3	6.76	5.97	18.66	6.31	8.72	6.08
N4	30.71	4.91	167.99	5.03	44.27	4.97
N5	12.51	4.99	40.44	5.09	16.92	5.03
N6	39.49	4.81	881.61	4.99	64.36	4.88
N7	48.03	4.62	190.55	4.88	66.57	4.70
N8	12.07	2.74	24.45	2.46	14.64	2.68
N9	20.36	4.50	130.32	4.81	30.27	4.60
N10	37.83	5.18	429.59	3.41	59.40	5.19

[a] Static, [b] Dynamic (1064 nm), [c] Dynamic (1907 nm)