Rationalizing the Suitability of Rhodamines as Chromophores in Dye-sensitized Solar Cells: A Systematic Molecular Design Study: Electronic Supplementary Information

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Table of Contents

S.1.	X-Ray Diffraction	S.2
S.2.	Nuclear Magnetic Resonance	S.3
S.3.	UV/vis Absorption Spectroscopy	S.7
S.4.	Cyclic Voltammetry	S.8
S.5.	Computational Studies	S.10
S.6.	Adsorption and Desorption studies	S.18
S.7.	DSC Fabrication	S.20

S.1. X-Ray Diffraction

Please refer to the electronic deposition material for more information about the structure of 1, 3 and 6.



Figure S.1. Relationship between the experimentally measured peak absorption energies, E_V, and the paraquinoidal HOSE contribution, C_{PQ}, calculated for the X-ray diffraction molecular geometries (1,3,6) and the DFT-optimized molecular geometries (1,3-7). Dyes 5 and 7 have similar energies and the same C_{PQ} contribution, appearing as a single data point on the DFT plot at 2.23 eV.





Figure S.2: ¹H NMR spectrum of 2 in deuterated methanol.



Figure S.3: ¹H NMR spectrum of 2 in deuterated DMSO.



Figure S.4: ¹³C NMR spectrum of **2** in deuterated methanol.



Figure S.5: ¹³C NMR spectrum of 2 in deuterated DMSO.

S.3.



Figure S.6: (*Left*) Experimental absorption spectrum of **4** in methanol at different concentrations. The curves have been normalized at the maximum absorption peak for easier comparison. (*Right*) Experimental absorption spectrum of **4** in different solvents at 0.0156 mM. The curves have been shifted (with acetone as reference) and normalized at the maximum absorption peak for easier comparison.



Figure S.7: (*Left*) Experimental absorption spectrum of **5** in methanol at different concentrations. The curves have been normalized at the maximum absorption peak for easier comparison. (*Right*) Experimental absorption spectrum of **5** in different solvents at 0.0156 mM. The curves have been shifted (with acetone as reference) and normalized at the maximum absorption peak for easier comparison.

S.7

S.4. Cyclic Voltammetry

The HOMO energy of each dye have be derived from their cyclic voltammograms in two different ways: the "onset" and the "peak" method. The first, employs Equation S.1 to find the HOMO energy by analyzing the onset potential of the oxidation peak:

$$E_{HOMO} = E_{[onset, oxidation vs. vacuum]}$$
(S.1)

The onset oxidation potential is a measure dependent to the reference electrode, Ag/AgCl. The conversion to vacuum can be carried out by shifting the voltage with respect to the standard hydrogen electrode (SHE) as reference:

$$0[V] vs. Ag/AgCl(3MKCl @ 20C)=0.21[V] vs. SHE$$
 (S.2)

The SHE reference can be converted to absolute electrode potential according to [1]:

$$0[V] vs. vacuum=4.281[V] vs. SHE$$
(S.3)

This value has to be corrected for the liquid junction potential in acetonitrile, which results in subtracting 0.093 V from the conversions with respect to the SHE and Ag/AgCl [2]. Therefore, the HOMO energy can be calculated as:

$$E_{HOMO} \left[eV \right] = - \left(E_{[onset, oxidation vs Ag/Cl]} + 4.398 \right) \left[eV \right]$$
(S.4)

The "peak" method can only be applied whenever the voltammogram shows both oxidation and reduction peaks for a single dye (e.g. Figure S.7(e,f)). This method approximates the HOMO energy level in the following fashion:

$$E_{HOMO} = |E_{[peak, oxidation vs. vacuum]} \cdot E_{[peak, oxidation vs. vacuum]}| / 2$$
 (S.5)

The "peak" approximation for rhodamine dyes returns values closer to the theoretically calculated values using DFT.



Figure S.8: Cyclic voltammograms for **1,3-7**, measured at four speeds: 100 mv/s, 75 mV/s, 50 mV/s and 25 mV/s. All plots show the second run of the cyclic voltammetry curve. (a) **1**, (b) **3**, (c) **4**, (d) **5**, (e) **6**, (f) **7**. The voltammograms of (f) were smoothened via a B'zier algorithm as the curves presented noise.

S.5. Computational Studies

A set of benchmarks was performed on **1-7** to determine the best computational method to study these molecules. Firstly, the effect of solvent on DFT and TD-DFT models was deemed necessary, because of the consistent shifts in energies caused by the inclusion of the PCM model. The recorded shifts were of ca. -2.3 eV in HOMO energies and ca. -0.15 eV in E_V . Secondly, the effect of the perchlorate counterion was studied on the geometries and lowest-vertical excitation energies calculated using DFT and TD-DFT in methanol using the PCM model. As shown in Table S.S.1, the counterion did not cause significant changes in the molecular geometries or values. In-house benchmarks over different TD-DFT functionals and LT-DF-LCC2 has shown that the LT-DF-LCC2 is a feasible model for small organic molecules, providing accurate results in absolute energies. A benchmark for **1-7** is shown on Figure S.8 and Table S.S.2. For this reason, E_V values were calculated using LT-DF-LCC2 with extended domains and cc-pVTZ auxiliary basis sets (JKFIT and MP2FIT)[3,4]. Solvent effects were included by subtracting the difference between the single-excitation CI (CI-Singles) calculation on excited states for the molecule in the gas phase and in methanol (PCM) from the LCC2-calculated excitation energy. CI-Singles calculations reduced the overestimation from experiments of $\Delta E_V = 0.15$ eV, on average, making LCC2 methods the most accurate model to calculate E_V for **1-7**.

Table S.1: Study of the effect of the counterion (sodium in **5** and perchlorate for **1,3,4,6,7**) on the geometries and energies calculated using DFT and TD-DFT with PCM (methanol). Difference in lowest-lying vertical excitation energies and RMSD deviations are calculated for **1,3-7** between the geometrically optimized dye containing (and lacking) the counterion. **2** is not an ion. The presence of the perchlorate counterion does not significantly affect geometries and energies. However, the presence of sodium affects energies and the geometry. For this reason, the sodium counterion was always included in all calculations involving **5**.

Dye	$\Delta \mathbf{E}_{\mathbf{V}} (\mathbf{B3LYP}) [\mathbf{eV}]$	$\Delta \mathbf{E}_{\mathbf{V}}$ (CAM-B3LYP) [eV]	RMSD (PBE1PBE) [Å]
1	0.00	0.00	0.04
3	0.00	0.01	0.15
4	0.00	0.00	0.10
5	0.91	1.58	0.69
6	0.00	0.00	0.01
7	0.01	0.01	0.12
7	0.01	0.01	0.12



Figure S.9: Benchmark of different models of theory compared to experimental values for **1-7**. Plot on the left shows benchmarks in gas phase. Plot on the right shows benchmarks in solution, using the PCM model.

Table S.2: Benchmark of different models of theory compared to experimental values for **1-7**. Starred models indicate that the result is for the molecules in solution (methanol). The 6-311+G(2d,p) basis set was used for all functionals. The calculations in solution were performed by applying the PCM model. Solution effects in LT-DF-LCC2 were provided by an energy shift calculated using the difference between the single-excitation CI (CI-Singles) calculation on excited states for the molecule in gas phase and in methanol (PCM). Experimental results were calculated from UV/vis absorption and fluorescence studies. Root-mean-squared-deviations (RMSD) and correlations between the calculations and the experimental results are reported. Despite its smaller correlation, LT-DF-LCC2 was the best performing functional compared to experiments. Deviations were the smallest across the range of molecules and it resulted to be the most reliable on larger sets of molecules of different classes after different in-house studies. All quantities shown are in eV.

	B3LYP	CAM-B3LYP	LCC2	B3LYP*	CAM-B3LYP*	LCC2*	Experimental*
1	3.05	3.24	2.90	2.89	3.05	2.67	2.49
2	-	-	-	-	-	2.43^{2}	2.39
3	2.88	3.08	2.69	2.76	2.94	2.53	2.35
4	2.70	2.91	2.44	2.58	2.79	2.30	2.28
5	-	-	2.55	2.58	2.79	2.29	2.23
6	2.65	2.83	2.36	2.53	2.70	2.22	2.19
7	2.73	2.95	2.47	2.62	2.83	2.34	2.23
RMSD	0.50	0.69	0.31	0.40	0.61	0.12	-
Correlation	97.57%	97.24%	94.74%	96.88%	95.89%	97.15%	-

2 Estimated from the dye \cdots TiO₂ system



Figure S.10: HOMO and LUMO Khon-Sham orbital plots of 1-7.



Figure S.11: Difference (LUMO²-HOMO²), HOMO, LUMO and LUMO+1 Khon-Sham orbital plots of **1** attached to a (TiO₂)₉ slab using two starting anchoring modes: bidentate bridging (*bb*) and bidentate chelating (*bc*). The geometry optimization of the system converged to a monodentate (*m*) structure for both starting structures.



Figure S.12: Difference (LUMO²-HOMO²), HOMO, LUMO and LUMO+1 Khon-Sham orbital plots of **2** attached to a (TiO₂)₉ slab using two anchoring modes: bidentate bridging (*bb*) and bidentate chelating (*bc*).



Figure S.13: Difference (LUMO²-HOMO²), HOMO, LUMO and LUMO+1 Khon-Sham orbital plots of **4** and **6** attached to a (TiO₂)₉ slab using two anchoring modes, respectively: bidentate bridging (*bb*) and bidentate chelating (*bc*).

Atom	x-position	y-position	z-position
Ti	15.6181	4.915257	15.538679
Ti	14.656039	6.531828	13.34211
Ti	17.613459	6.270851	13.08594
Ti	14.907321	7.679475	15.89544
Ti	20.75371	6.862666	12.242809
Ti	18.144937	4.270597	15.519405
Ti	20.762607	5.138394	14.77007
Ti	17.901846	7.483138	15.838273
Ti	21.136004	8.061333	15.539596
0	14.320878	4.940144	14.100751
0	16.506931	3.427434	16.089748
0	15.998929	6.52309	12.119939
0	16.415538	8.474763	16.506535
0	13.865553	7.895651	14.349067
0	14.579851	6.088665	16.664016
0	21.360157	5.298375	13.036662
0	17.128385	4.584195	13.950862
0	19.874559	3.641029	15.478823
0	19.05209	5.949794	14.72939
0	21.668387	6.23336	15.834641
0	18.97042	6.233881	11.96149
0	17.978321	8.085584	13.904925
0	20.702593	8.038422	13.60583
0	17.393451	5.716852	16.531218
0	22.237354	9.17945	15.984697
0	19.397398	8.19721	16.403101
0	16.051565	6.719305	14.671194

Table S.3: Initial atomic positions for DFT geometry optimization of the (TiO₂)₉ slab

Table S.4: First 8 singlet-singlet TD-DFT excitations for 1 (*bc*)(converged to *m*) adsorbed on a $(TiO_2)_9$ slab with corresponding energy, wavelength (λ), oscillator strength (f) and composition. In this table, HOMO and LUMO energy levels correspond to the 257th and 258th molecular orbitals, respectively, that are presented in order of increasing energy.

	Energy			
n	(eV)	λ (nm)	f	Composition
1	2.85	436	0.6210	98.2% (257 -> 258)
2	3.01	412	0.0001	99.5% (257 -> 259)
3	3.18	390	0.0003	98.9% (257 -> 260)
4	3.20	387	0.0005	96.3% (256 -> 258)
5	3.27	380	0.0001	97.7% (257 -> 261)

6	3.36	369	0.0010	94.4% (257 -> 262), 2.6% (257 -> 264) 95.3% (257 -> 263), 2.2% (257 ->
7	3.44	360	0.0001	265)
8	3.46	359	0.0095	97.3% (255 -> 258)

Table S.5: First 8 singlet-singlet TD-DFT excitations for 1 (*bb*)(converged to *m*) adsorbed on a $(TiO_2)_9$ slab with corresponding energy, wavelength (λ), oscillator strength (f) and composition. In this table, HOMO and LUMO energy levels correspond to the 257th and 258th molecular orbitals, respectively, that are presented in order of increasing energy.

	Energy			
n	(eV)	λ (nm)	f	Composition
1	2.86	433	0.6389	97.7% (257 -> 258)
2	3.17	392	0.0012	97.9% (257 -> 259)
3	3.22	386	0.0022	94.0% (256 -> 258), 2.1% (257 -> 260)
				79.7% (257 -> 260), 14.8% (257 -> 261), 2.5% (256 ->
4	3.22	385	0.0152	258)
5	3.34	372	0.0001	83.1% (257 -> 261), 15.3% (257 -> 260)
				58.3% (257 -> 262), 30.9% (257 -> 263), 8.7% (257 ->
6	3.43	362	0.0010	264)
				44.6% (257 -> 263), 40.2% (257 -> 262), 11.7% (257 ->
7	3.44	361	0.0002	264)
8	3.55	350	0.0005	76.9% (257 -> 264), 19.9% (257 -> 263)

Table S.6: First 8 singlet-singlet TD-DFT excitations for **2** (*bc*) adsorbed on a (TiO₂)₉ slab with corresponding energy, wavelength (λ), oscillator strength (f) and composition. In this table, HOMO and LUMO energy levels correspond to the 281th and 282th molecular orbitals, respectively, that are presented in order of increasing energy.

	Energy			
n	(eV)	λ (nm)	f	Composition
1	2.69	461	0.8065	98.3% (281 -> 282)
2	3.00	414	0.0243	56.8% (281 -> 283), 41.7% (281 -> 284)
				55.5% (281 -> 284), 41.1% (281 -> 283), 2.1% (281 ->
3	3.10	399	0.0018	285)
4	3.16	393	0.0005	96.7% (281 -> 285)
5	3.16	392	0.0012	94.2% (280 -> 282), 3.9% (279 -> 282)
6	3.31	375	0.0003	93.6% (281 -> 286), 4.6% (281 -> 288)
7	3.34	371	0.0001	97.2% (281 -> 287)
				87.4% (281 -> 288), 5.2% (281 -> 286), 2.4% (281 ->
8	3.44	360	0.0008	292)

Table S.7: First 8 singlet-singlet TD-DFT excitations for **2** (*bb*) adsorbed on a (TiO₂)₉ slab with corresponding energy, wavelength (λ), oscillator strength (f) and composition. In this table, HOMO and LUMO energy levels correspond to the 281th and 282th molecular orbitals, respectively, that are presented in order of increasing energy.

	Energy			
n	(eV)	λ (nm)	f	Composition
1	2.70	460	0.7192	95.7% (281 -> 282), 2.9% (281 -> 283)
2	2.81	442	0.0558	95.9% (281 -> 283), 3.0% (281 -> 282)
3	3.08	402	0.0034	97.9% (281 -> 284)
4	3.17	391	0.0019	94.5% (280 -> 282), 4.0% (279 -> 282)
5	3.26	381	0.0003	86.9% (281 -> 285), 7.9% (281 -> 286), 3.1% (281 -> 287)
6	3.30	376	0.0015	86.7% (281 -> 286), 7.1% (281 -> 285), 3.7% (281 -> 288)
7	3.36	369	0.0001	90.7% (281 -> 287), 2.9% (281 -> 285), 2.3% (281 -> 289)
				86.5% (281 -> 288), 4.1% (281 -> 290), 2.5% (281 -> 287), 2.5%
8	3.41	363	0.0037	(281 -> 286)

Table S.8: First 8 singlet-singlet TD-DFT excitations for **4** (*bb*) adsorbed on a (TiO₂)₉ slab with corresponding energy, wavelength (λ), oscillator strength (f) and composition. In this table, HOMO and LUMO energy levels correspond to the 289th and 290th molecular orbitals, respectively, that are presented in order of increasing energy.

	Energy			
n	(eV)	λ (nm)	F	Composition
1	2.57	482	0.8123	97.5% (289 -> 290)
2	2.70	459	0.0380	97.2% (289 -> 291)
3	2.99	414	0.0027	97.8% (289 -> 292)
4	3.06	406	0.0204	91.8% (288 -> 290), 6.3% (287 -> 290)
5	3.19	389	0.0003	77.8% (289 -> 293), 18.1% (289 -> 294)
6	3.21	386	0.0018	77.0% (289 -> 294), 16.4% (289 -> 293), 2.9% (289 -> 296)
7	3.29	377	0.0001	92.2% (289 -> 295), 2.9% (289 -> 296)
				83.0% (289 -> 296), 5.0% (289 -> 298), 2.9% (289 -> 297), 2.9% (289
8	3.33	372	0.0036	-> 295), 2.7% (289 -> 293)

Table S.9: First 8 singlet-singlet TD-DFT excitations for **6** (bc) adsorbed on a $(TiO_2)_9$ slab with corresponding energy, wavelength (λ), oscillator strength (f) and composition. In this table, HOMO and LUMO energy levels correspond to the 301th and 302th molecular orbitals, respectively, that are presented in order of increasing energy.

	Energy			
n	(eV)	λ (nm)	F	Composition
1	2.46	504	0.8160	96.3% (301 -> 302) 48.1% (301 -> 303), 32.0% (301 -> 305), 16.5% (301 -> 304),
2	2.65	468	0.0679	2.7% (301 -> 302)
3	2.72	456	0.0116	46.2% (301 -> 303), 38.7% (301 -> 304), 13.3% (301 -> 305)

4	2.76	449	0.0029	51.8% (301 -> 305), 42.95% (301 -> 304), 4.3% (301 -> 303
5	2.90	428	0.0068	93.2% (300 -> 302), 5.6% (299 -> 302)
6	2.92	425	0.0003	96.8% (301 -> 306), 2.5% (301 -> 308)
7	2.94	421	0.0001	98.5% (301 -> 307)
8	3.05	406	0.0008	92.8% (301 -> 308), 2.8% (301 -> 309), 2.7% (301 -> 306)

Table S.10: First 8 singlet-singlet TD-DFT excitations for **6** (bb) adsorbed on a $(TiO_2)_9$ slab with corresponding energy, wavelength (λ), oscillator strength (f) and composition. In this table, HOMO and LUMO energy levels correspond to the 301th and 302th molecular orbitals, respectively, that are presented in order of increasing energy.

	Energy			
n	(eV)	λ (nm)	f	Composition
1	2.58	601	0.8048	99.25841408% (301 -> 302)
2	2.29	543	0.0001	98.52991442% (301 -> 303)
3	2.36	525	0.0004	97.20920178% (301 -> 304)
				93.09847058% (301 -> 305), 4.03% (301 ->
4	2.43	510	0.0012	307)
				90.62887712% (301 -> 307), 4.35% (301 ->
5	2.49	499	0.0011	305)
				89.90332232% (300 -> 302), 4.61% (299 ->
6	2.56	484	0.0014	302)
7	2.06	480	0.0001	96.07197728%, (301 -> 306)
8	2.61	475	0.0166	93.30872832% (301 -> 308)

S.6.

Adsorption and Desorption studies



Figure S.14: Amount of dye adsorbed on a 0.16 cm TiO_2 surface as a function of adsorption time, for singly-sensitized **1**, **N719** and **8**. The dye loading was calculated by measuring the intensity of the maximum peak absorption via UV/vis spectroscopy of the adsorbed titania layer. The maximum peak absorption for **1**, **N719** and **8** were 505 nm, 542 nm and 640 nm, respectively. Two TiO₂ layers were measured for each dye and sensitization time, and the results were averaged. Adsorption intensity was measured at 1.25, 2.5, 5, 10, 20, 40, 80, 160, 320, 640 minutes.



Figure S.15: Amount of dye desorbed from a 0.16 cm TiO₂ surface as a function of desorption time, for previously singly-sensitized **1** (2 hours), **N719** (24 hours) and **8** (2 hours). The dye loading was calculated by measuring the intensity of the maximum peak absorption via UV/vis spectroscopy of the desorbed dye solution. The maximum peak absorption for **1**, **N719** and **8** were 499 nm, 512 nm and 497 nm, respectively. Desorption was measured at: 0.25, 0.5, 0.75, 1, 2, 3, 4, 5, 10, 20, 40, 80, 160 minutes.

S.7. DSC Fabrication



Figure S.16: J-V curves for the N719 benchmarked cells, as described in Table S.S..

Table S.11: Benchmark of fabricated DSC performance for 16 cells with a ruthenium dye, **N719**. Measured values include: short-circuit current, I_{SC} , short-circuit current density, J_{SC} , open-circuit voltage V_{OC} , fill factor, *FF*, power and power conversion efficiency, η .

Cell	Isc [mA]	Jsc [mA cm ⁻²]	Voc [mV]	FF[%]	Power[mW]	η[%]
1	-1.15	7.17	638	69	0.51	3.2
2	-0.95	5.93	604	58	0.33	2.1
3	-1.02	6.35	630	66	0.42	2.6
4	-0.93	5.83	632	65	0.38	2.4
5	-1.4	8.76	650	70	0.64	4.0
6	-1.17	7.33	626	68	0.5	3.1
7	-1.27	7.92	624	67	0.53	3.3
8	-1.18	7.41	616	66	0.48	3.0
9	-1.29	8.07	652	67	0.56	3.5
10	-1.72	10.73	652	71	0.79	5.0
11	-1.18	7.35	642	71	0.53	3.3
12	-1.28	7.99	630	67	0.54	3.4
13	-1.41	8.84	660	70	0.65	4.1
14	-1.54	9.62	640	67	0.66	4.2
15	-1.49	9.32	644	68	0.66	4.1
16	-1.17	7.31	640	68	0.51	3.2
Average	-1.26	7.87	636	67	0.54	3.4



Figure S.17: DSC characteristics of the benchmarked N719 cells, as described in Table S.S.. From top left to bottom right: current density, J_{SC} , open-circuit voltage V_{OC} , fill factor, *FF*, power conversion efficiency, η .

Table S.12: DSC device performance of rhodamines, **1-6**, fluorescein, **8** and ruthenium dye, **N3**, as a standard dye. All dyes except for the standard **N3** dye produced a negligible power conversion efficiency.

Dyes	Isc [mA]	Jsc [mA cm ⁻²]	Voc[mV]	FF[%]	Power[mW]	η[%]
1	-0.01	0.03	73	37	0.00	0
1	-0.02	0.10	123	31	0.00	0
1	-0.01	0.05	63	25	0.00	0
1	0	0.02	45	36	0.00	0
1	0	0.03	79	29	0.00	0
2	-0.01	0.06	7	19	0.00	0
2	-0.01	0.03	5	12	0.00	0
2	-0.01	0.04	17	24	0.00	0
3	-0.01	0.05	69	25	0.00	0
3	0	0.02	147	24	0.00	0
3	0	0.02	145	21	0.00	0
3	-0.01	0.04	5	21	0.00	0
4	-0.02	0.11	167	22	0.00	0
4	-0.01	0.03	105	28	0.00	0
5	-0.01	0.06	205	29	0.00	0
5	0	0.03	183	40	0.00	0
6	0	0.01	77	29	0.00	0
6	0	0.01	93	28	0.00	0
6	0	0.01	81	25	0.00	0
8	-0.05	0.27	143	33	0.00	0
8	-0.05	0.31	145	31	0.00	0
1+5	0.01	0.05	269	64.69	0.00	0
1+7	0.01	0.05	229	41.73	0.00	0
1+7	0.01	0.06	147	32.05	0.00	0
1+7	0.01	0.05	187	46.57	0.00	0
1+7	0.01	0.07	223	40.69	0.00	0
1+7	0.01	0.05	243	41.27	0.00	0
5+8	0.02	0.13	277	87.98	0.00	0
5+8	0.02	0.15	429	80.73	0.01	0
5+8	0.01	0.07	377	68.66	0.00	0
5+8	0.02	0.12	423	67.43	0.01	0
5+8	0.02	0.13	427	85.3	0.01	0
N3	-1.44	9.01	610	51	0.45	2.
N3	-1.65	10.33	640	69	0.73	4.
N3	-1.47	9.18	638	65	0.61	3.
N3	-1.5	9.37	628	65	0.62	3.



Figure S.18: J-V curves for the sequentially co-sensitized cells, **1** or **2** with **N3**, as described in Table S.S..

Table S.13: Detailed performances of sequentially co-sensitized dyes 1 or 2 with N3. Five cells for each dye pairing were tested and averaged out.

Dyes	Isc [mA]	J _{SC} [mA cm ⁻²]	Voc [mV]	FF[%]	Power[mW]	η[%]
$1 \rightarrow N3$	-1.28	7.99	582	69	0.51	3.2
$1 \rightarrow N3$	-0.64	3.99	558	66	0.24	1.5
$1 \rightarrow N3$	-0.55	3.45	534	63	0.19	1.2
$1 \rightarrow N3$	-0.66	4.14	564	62	0.23	1.5
$2 \rightarrow N3$	-1.29	8.08	620	70	0.56	3.5
$2 \rightarrow N3$	-1.2	7.52	600	70	0.51	3.2
$2 \rightarrow N3$	-1.02	6.36	582	68	0.40	2.5
$2 \rightarrow N3$	-0.83	5.17	584	66	0.32	2.0
$2 \rightarrow N3$	-0.99	6.16	588	68	0.39	2.5

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