Electronic Supplementary Information

Acid-base properties of the N3 Ruthenium(II) solar cell sensitizer: A combined experimental and computational analysis

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Table S1. HOMOs and LUMOs energies (eV) of N3Hx molecules in water solution.

	$N3H_4$	$N3H_3^-$		$N3H_2^{2-}$				$N3H^{3-}$		$N3^{4-}$
		A	B	A	B	C	D	A	B	
H-6	-6.98	-6.76	-6.77	-6.65	-6.65	-6.64	-6.67	-6.39	-6.39	-6.35
H-5	-6.86	-6.73	-6.74	-6.41	-6.43	-6.42	-6.46	-6.38	-6.38	-6.35
H-4	-6.84	-6.45	-6.46	-6.40	-6.42	-6.42	-6.46	-6.37	-6.38	-6.34
H-3	-6.29	-6.25	-6.25	-6.21	-6.21	-6.21	-6.20	-6.16	-6.17	-6.11
H-2	-5.90	-5.82	-5.82	-5.73	-5.72	-5.71	-5.73	-5.62	-5.61	-5.50
H-1	-5.87	-5.78	-5.79	-5.68	-5.68	-5.66	-5.69	-5.57	-5.57	-5.45
H	-5.65	-5.57	-5.54	-5.46	-5.45	-5.47	-5.44	-5.33	-5.35	-5.23
L	-3.16	-3.07	-3.05	-2.99	-2.86	-2.89	-2.84	-2.76	-2.77	-2.35
L+1	-3.07	-2.87	-2.87	-2.50	-2.79	-2.74	-2.82	-2.38	-2.39	-2.29
L+2	-2.62	-2.54	-2.54	-2.43	-2.13	-2.15	-2.14	-2.07	-2.07	-1.58
L+3	-2.58	-2.19	-2.17	-2.06	-2.10	-1.70	-2.10	-1.67	-1.64	-1.53
L+4	-2.22	-2.07	-2.10	-1.64	-1.72	-1.60	-1.74	-1.57	-1.58	-1.51
L+5	-2.07	-1.69	-1.69	-1.54	-1.57	-0.53	-1.54	-1.43	-1.46	-1.34
L+6	-0.79	-0.69	-0.68	-0.62	-0.52	-0.39	-0.52	-0.41	-0.42	-0.12

Table S2. Values of ΔGvac (kcal/mol), ΔΔGsolv (kcal/mol) of the N3 complexes and calculated pK$_a$s using different computational methods.

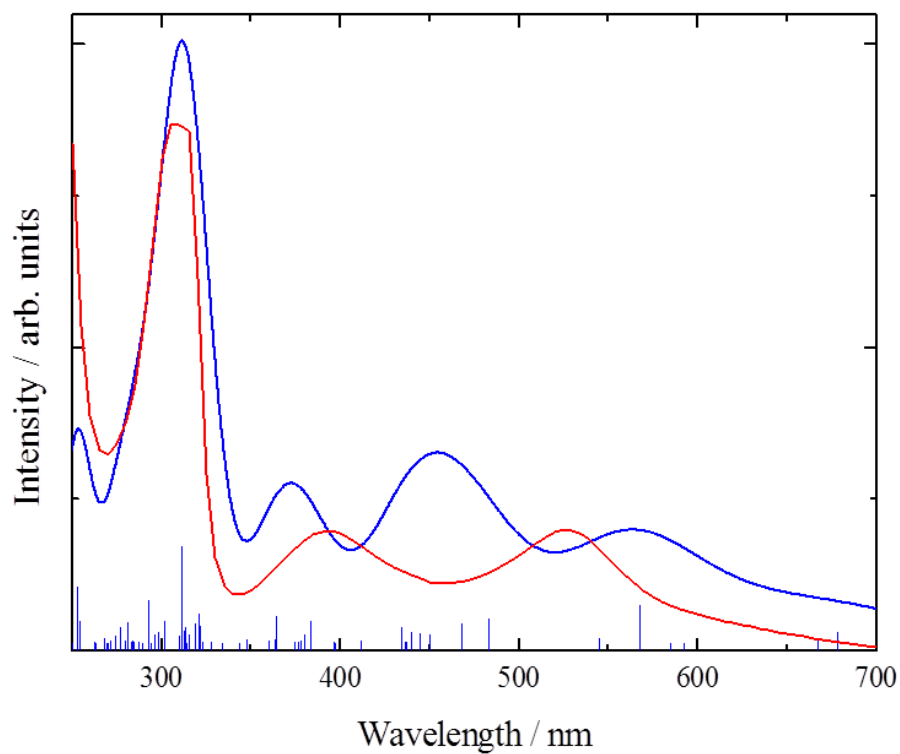|	Δgvac	ΔΔGsol UA0	pKa UA0	ΔΔGsol SPH	pKa SPH	ΔΔGsol UAHF	pKa UAHF
$N3H_4/ N3H_3^-\_A$	310.62	-34.68	5.55	-40.01	1.64	-38.56	2.71
$N3H_4/ N3H_3^-\_B$	308.21	-31.77	5.91	-37.16	1.96	-35.6	3.11
$N3H_3^-\_A/ N3H_2^{2-}\_A$	349.78	-72.37	6.63	-77.78	2.66	-75	4.70
$N3H_3^-\_A/ N3H_2^{2-}\_B$	345.09	-67.04	7.09	-72.66	2.97	-69.87	5.02
$N3H_3^-\_A/ N3H_2^{2-}\_C$	344.80	-67.29	6.70	-72.61	2.80	-70.03	4.69
$N3H_3^-\_B/ N3H_2^{2-}\_A$	352.19	-75.28	6.26	-80.63	2.34	-77.96	4.30
$N3H_3^-\_B/ N3H_2^{2-}\_D$	346.42	-68.57	6.95	-74.03	2.95	-71.23	5.00
$N3H_2^{2-}\_A/ N3H^{3-}\_A$	383.57	-103.80	8.35	-109.24	4.37	-106.17	6.62
$N3H_2^{2-}\_A/ N3H^{3-}\_B$	381.65	-101.92	8.32	-107.34	4.35	-104.53	6.41
$N3H_2^{2-}\_B/ N3H^{3-}\_A$	388.26	-109.13	7.89	-114.36	4.05	-111.3	6.30
$N3H_2^{2-}\_C/ N3H^{3-}\_B$	386.63	-107.00	8.25	-112.51	4.21	-109.5	6.42
$N3H_2^{2-}\_D/ N3H^{3-}\_A$	389.34	-110.51	7.67	-115.84	3.74	-112.9	5.91
$N3H^{3-}\_A/ N3^{4-}$	424.15	-143.27	9.17	-148.62	5.24	-145.49	7.54
$N3H^{3-}\_B/ N3^{4-}$	426.06	-145.15	9.19	-150.52	5.26	-147.13	7.74

Figure S1. Comparison between computed (blue line) and experimental (red line) spectrum of $N3H_4$. Blue vertical lines correspond to calculated excitation energies and oscillator strengths for $N3H_4$.
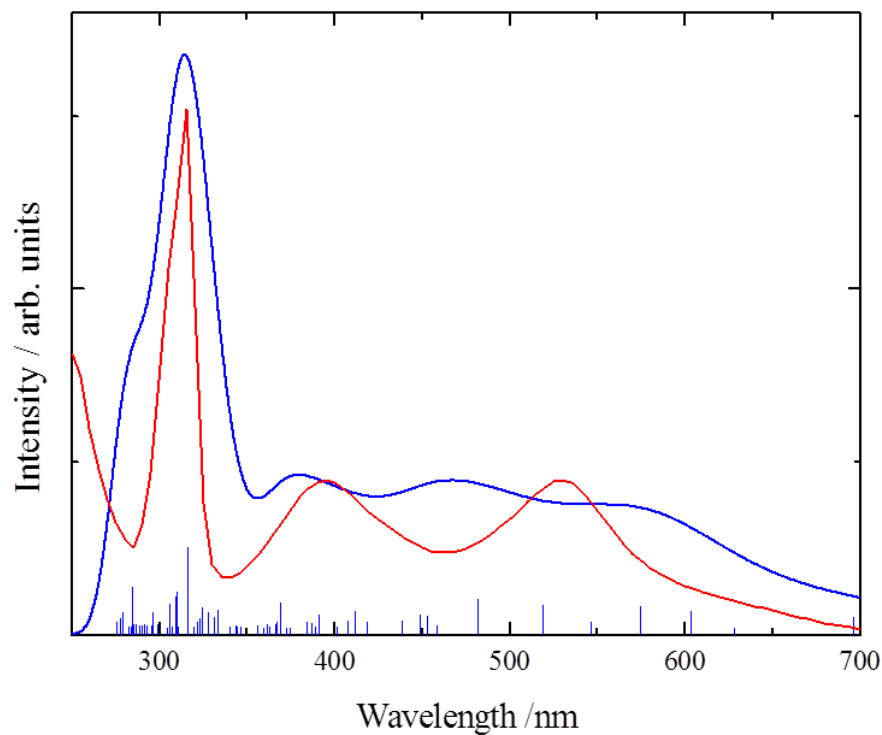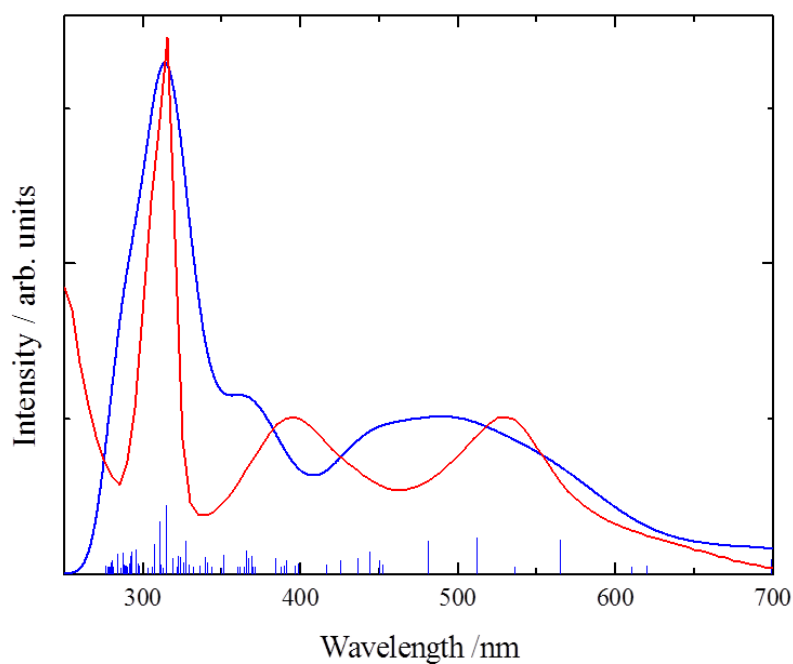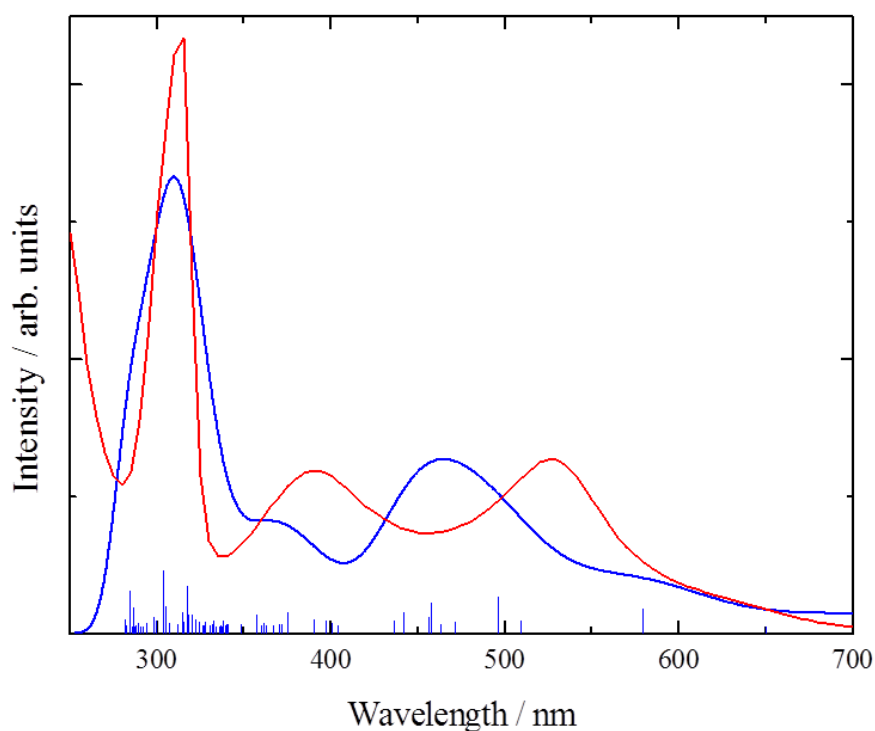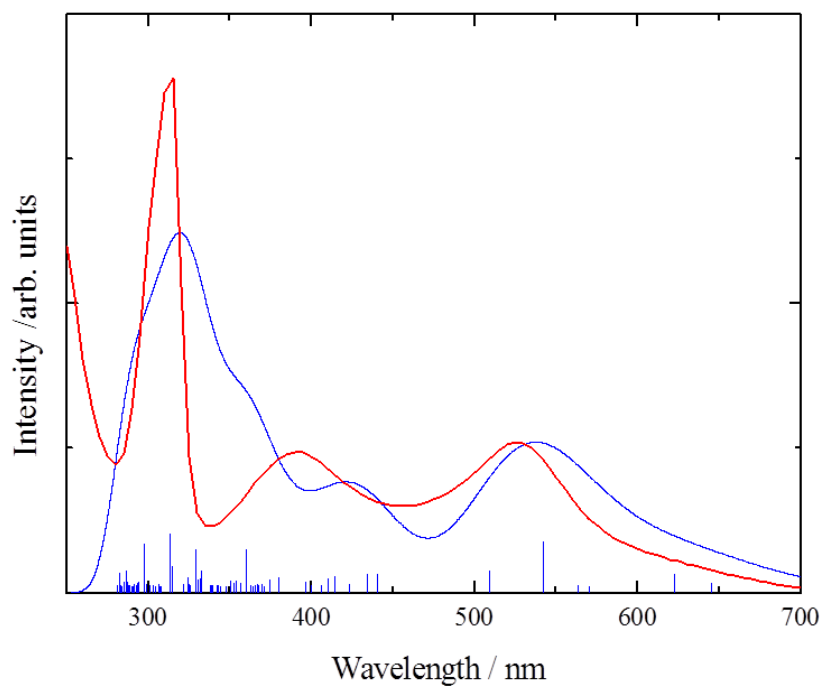

Figure S2. Comparison between computed (blue line) and experimental (red line) spectrum of $N3H_3^-\_A$. Blue vertical lines correspond to calculated excitation energies and oscillator strengths for $N3H_3^-\_A$.

Figure S3. Comparison between computed (blue line) and experimental (red line) spectrum of N3H$_3^-$_B. Blue vertical lines correspond to calculated excitation energies and oscillator strengths for N3H$_3^-$_B.
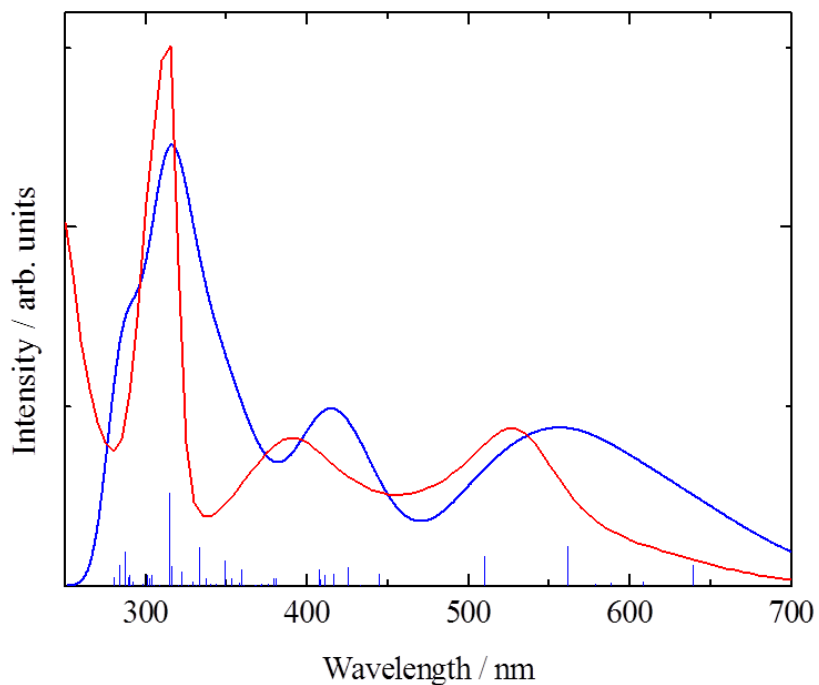

Figure S4. Comparison between computed (blue line) and experimental (red line) spectrum of N3H$_2^{2-}$_A. Blue vertical lines correspond to calculated excitation energies and oscillator strengths for N3H$_2^{2-}$_A.

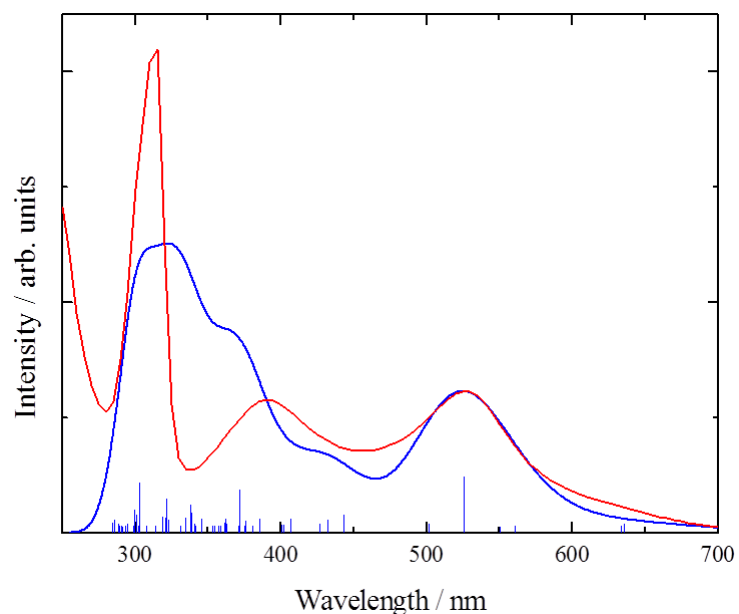**Figure S5.** Comparison between computed (blue line) and experimental (red line) spectrum of $N3H_2^{2-}$_B. Blue vertical lines correspond to calculated excitation energies and oscillator strengths for $N3H_2^{2-}$_B.

Figure S6. Comparison between computed (blue line) and experimental (red line) spectrum of $N3H_2^{2-}$_C. Blue vertical lines correspond to calculated excitation energies and oscillator strengths for $N3H_2^{2-}$_C.
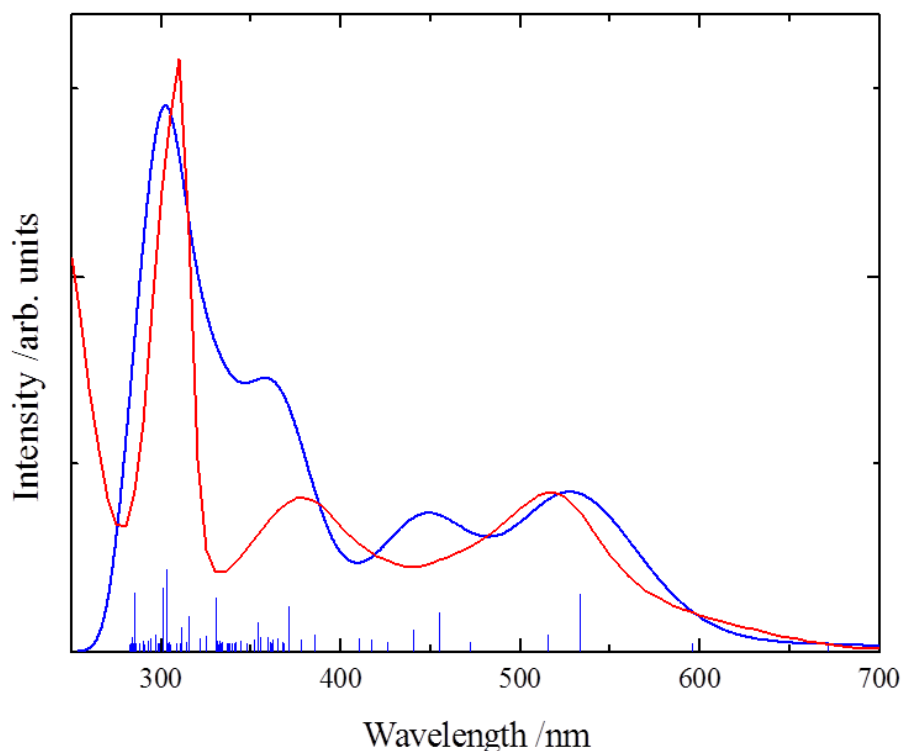
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Figure S7. Comparison between computed (blue line) and experimental (red line) spectrum of $N3H_2^{2-}\_D$. Blue vertical lines correspond to calculated excitation energies and oscillator strengths for $N3H_2^{2-}\_D$.
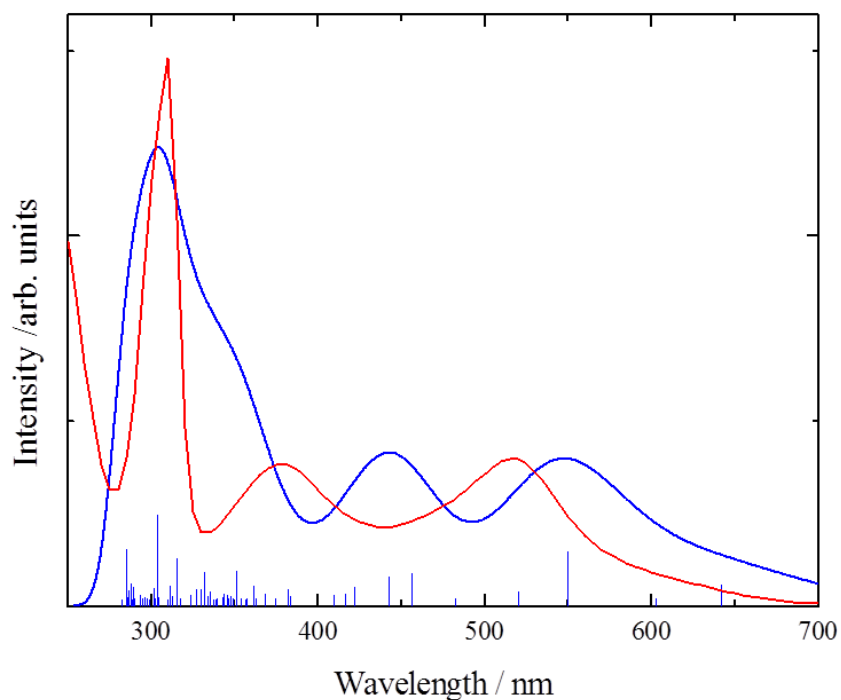
Figure S8. Comparison between computed (blue line) and experimental (red line) spectrum of $N3H^{3-}\_A$. Blue vertical lines correspond to calculated excitation energies and oscillator strengths for $N3H^{3-}\_A$.

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Figure S9. Comparison between computed (blue line) and experimental (red line) spectrum of N3H^{3-}_B. Blue vertical lines correspond to calculated excitation energies and oscillator strengths for N3H^{3-}_B.
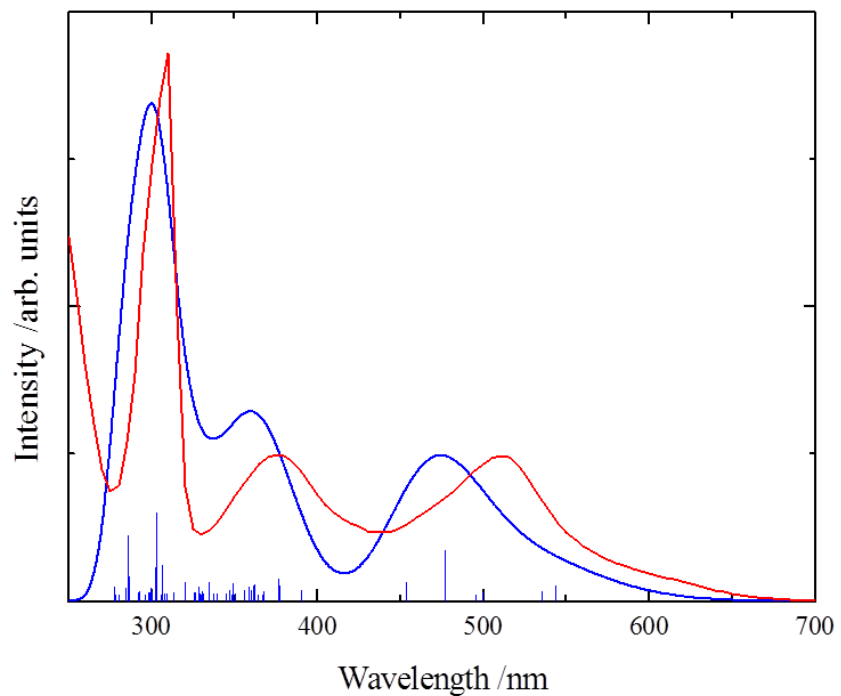

Figure S10. Comparison between computed (blue line) and experimental (red line) spectrum of N3^{4-}. Blue vertical lines correspond to calculated excitation energies and oscillator strengths for N3^{4-}.