Supporting Material

Primary reactions of the LOV2 domain of phototropin studied with ultrafast mid-infrared spectroscopy and quantum chemistry

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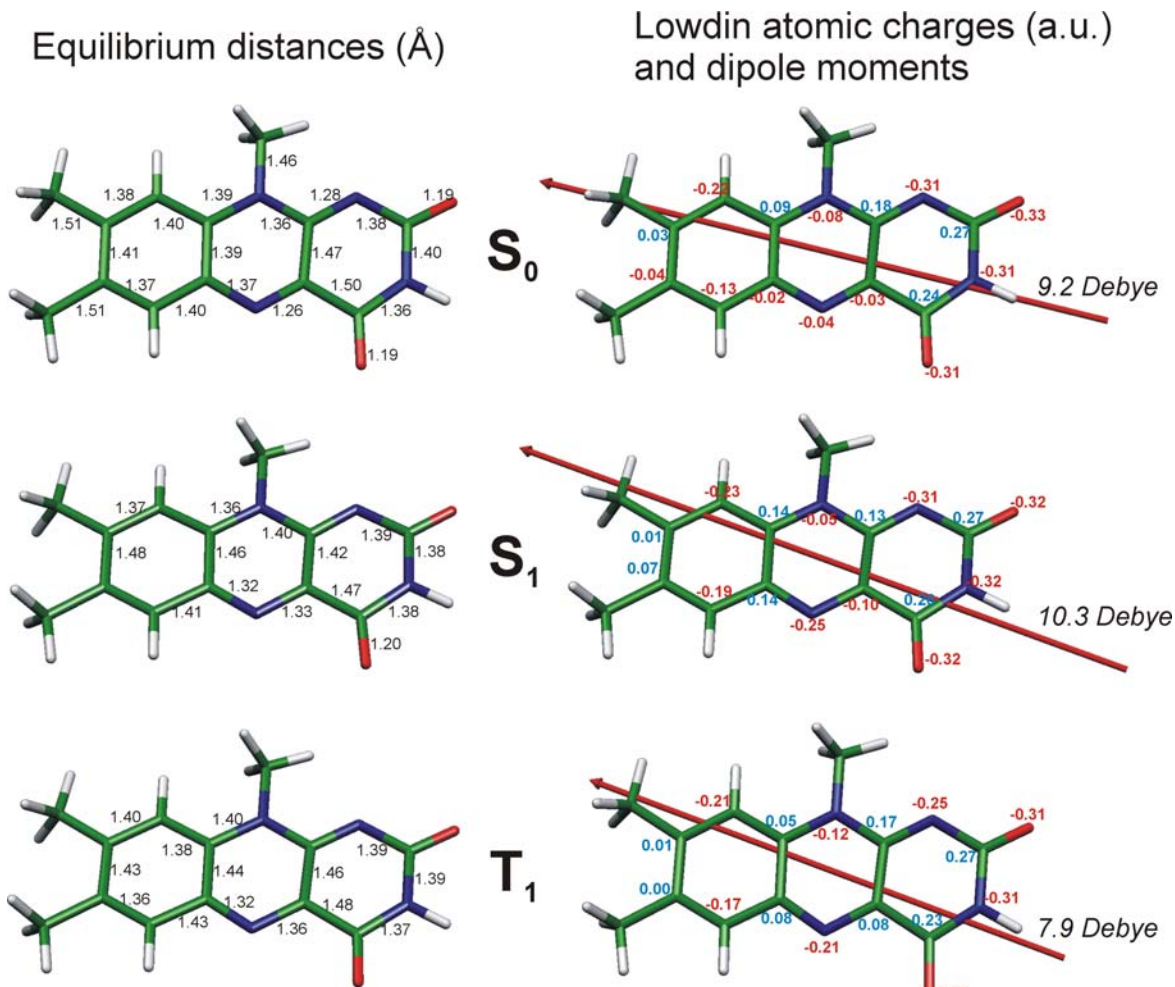
Fig. S1. Optimized structure, atomic charges, and dipole moment of lumiflavin in the ground state computed by HF/6-31G(d) and excited S_1 and T_1 states computed by CIS/6-31G(d). In the excited state structures only distances that are different from those in the ground state are indicated.
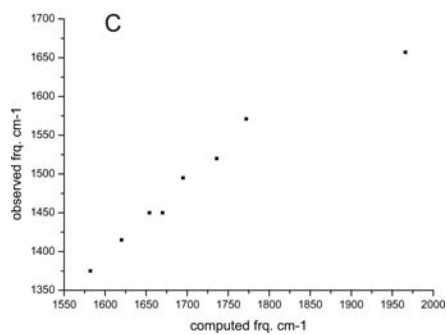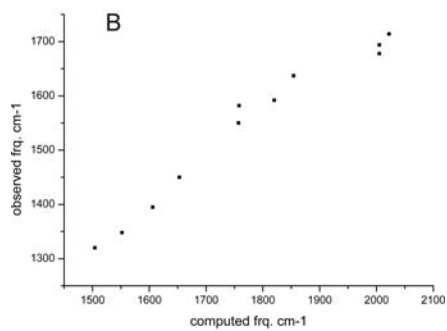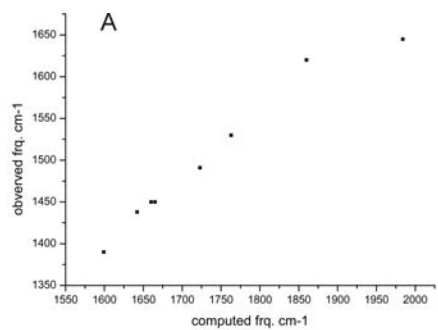
Fig. S2. Correspondence between observed and computed vibrational frequencies:
A. ground state, HF/6-31(d)G method, Table S1;
B. S$_1$ state, CIS/6-31(d)G method, Table S2;
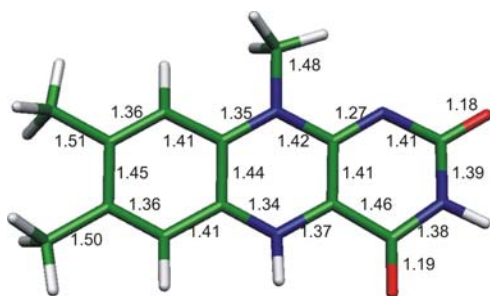C. T$_1$ state, CIS/6-31G(d) method, Table S3.

Fig. S3. Optimized structure of the N(5)-H protonated lumiflavin cation in the T_1 state computed by CIS/6-31G(d).

Table S1. Assignment of the experimental electronic ground state frequencies to the HF/6-31G(d) harmonic normal modes.

Comput. freq. (IR intensity)	Normal mode major components, ν – stretch, δ – bend	Exptl. freq.
2022 (8.5)	ν C(4)=O, C(2)=O	1714, 1694
2005 (25.9)	ν C(2)=O, C(4)=O	1678
1854 (14.4)	ν C6C7, C9C9a, C9aN10, N5C4a, C10aN1	1637
1820 (7.5)	ν C6C7, C6C5a, C8C9, C9aN10, N5C4a	1582
1758 (30.0)	ν C10aN1, N5C4a, C6C7	1550
1757 (4.9)	ν C7C8, C5aC9a, N10C10a, C10aN1, C5aN5, N5C4a	1550
1677 (0.1)	δ CH$_3$(N10,C^{I},C^{II}); ν C7C8, C9C9a, C9aN10, C5aN5, N10C10a	
1660 (0.3)	δ CH$_3$(N10)	
1653 (1.9)	δ CH$_3$(N10,C^{I}); ν C9aN10, C5aC9a, N5C4a, C4aC4	(1450)
1642 (0.8)	δ CH$_3$(C^{II}); ν C9C9a, C9aN10, C6C5a, C6C7	
1639 (0.4)	δ CH$_3$(C^{I},C^{II})	
1637 (0.1)	δ CH$_3$(C^{I}); ν C6C5a, C9C9a, C7C8, C8C9, C5aN5	
1624 (0.0)	δ CH$_3$(C^{I},C^{II})	
1606 (1.0)	δ CH$_3$(N10); ν C8C9, C9aN10, N10C10a	1395
1591 (0.2)	δ CH$_3$(N10,C^{I},C^{II}); ν C6C7, C6C5a, C8C9, C9C9a, C9aN10, N10C10a, C5aN5, N5C4a	
1576 (0.1)	δ CH$_3$(C^{I},C^{II})	
1572 (0.3)	δ CN3H; ν C4aC10a; C10aN1, C4aC4	
1563 (0.3)	δ CH$_3$(C^{I},C^{II}); ν C4aC4, C5aN5, N10C10a, N1C2, C2N3, N3C4	
1552 (5.2)	δ CH$_3$(N10), CN3H; ν C4aC10a, N10C(CH$_3$), C4aC4, C4N3, N3C2, C2N1	1348
1504 (2.8)	ν C8C9, C9C9a, N10C(CH$_3$), N10C10a, C4N3, N3C2, C2N1	1320

Table S2. Assignment of the S_1 experimental frequencies to the CIS/6-31G(d) harmonic normal modes.

Comput. frq. cm^{-1}, (IR intensity)	Normal mode major components, ν – stretch, δ – bend	Exptl. frq. cm^{-1}
1988 (23.1)	ν C(2)=O	1657
1966 (14.9)	ν C(4)=O	1657
1772 (9.1)	ν C8C9, C7C6, C6C5a, C9aN10, C10aN1	1570
1736 (3.5)	ν C8C9, C7C6, C10aN1	1520
1695 (2.8)	ν C6C7, C5aC9a, C9aN10, C4aC10a	1495
1670 (4.0)	ν N5C5a, N5C4a, C9aN10	1475
1654 (3.4)	ν C7C8, C6C5a, C9C9a, C9aN10, N5C5a	1475
1653 (0.3)	δ CH$_3$(N10)	
1652 (0.7)	δ CH$_3$(N10); ν N5C5a, N5C4a, N10C10a	
1634 (0.4)	δ CH$_3$(C^I,C^{II})	
1622 (0.6)	δ CH$_3$(C^I,C^{II}); ν N5C4a, C10aN1	
1620 (1.4)	δ CH$_3$(C^{II}); ν C7C8, C9C9a, C6C5a, N5C4a	1415
1618 (0.0)	δ CH$_3$(C^I,C^{II})	
1606 (0.6)	δ CH$_3$(N10); ν C9aN10, N5C4a, C10aN1, C2N3	
1582 (1.3)	δ CH$_3$(N10); ν C9aN10, C10aN1, N1C2, C2N3, N3C4, C4C4a, N5C4a	1375
1572 (0.7)	ν C8C9, C7C6, C10aN1, C9aN10	
1567 (0.7)	δ CN3H; ν C4aN5, C10aN1, C2N3	
1559 (0.1)	δ CH$_3$(C^I,C^{II})	
1529 (5.4)	ν C4aC10a, N10C(CH$_3$), C7C6, C6C5a, C2N1, N3C4	
1519 (3.6)	ν C9aN10, C5aN5, C10aN1, C4aC4, N3C4, N3C2	

Table S3. Assignment of the T_1 experimental frequencies to the CIS/6-31G(d) harmonic normal modes.

Comput. frq. cm^{-1}, (IR intensity)	Normal mode major components, ν – stretch, δ – bend	Exptl. frq. cm^{-1}
2012 (16.2)	ν C(2)=O	1660, 1645
1984 (12.5)	ν C(4)=O	1660, 1645
1860 (1.3)	ν C10aN1, C5aN5, N5C4a	1620
1763 (11.0)	ν C7C6, C8C9, C9aN10, C10aN10, N5C4a, C10aN1	1530
1723 (29.0)	ν C7C6, C8C9, C9aN10, C5aN5, C10aN1	1491
1665 (1.7)	δ CH$_3$(N10); ν C8C9, N10C10a, C10aN1	1475
1660 (2.6)	ν C7C8, C9C9a, C9aN10, C6C5a, C5aN5	1475
1656 (0.2)	δ CH$_3$(N10)	
1642 (1.7)	ν C7C6, C5aC9a, C9aN10, C4aC10a, C10aN1	1438
1637 (0.4)	δ CH$_3$(C^I,C^{II})	
1628 (0.1)	δ CH$_3$(C^I,C^{II}); ν C7C6, C8C7, C8C9, C9aN10, N5C4a, N10C10a	
1622 (0.0)	δ CH$_3$(C^I,C^{II});	
1619 (1.8)	δ CH$_3$(N10,C^I,C^{II}); ν C7C8, C5aC9a, C9C9a, ,C6C5a, N10C10a	
1599 (1.6)	ν C8C9, C9C9a, C7C6, C6C5a, C9aN10, N10C10a, N5C4a	1390
1580 (1.0)	ν C8C9, C9C9a, C7C6, C6C5a, C9aN10, N10C10a, C5aN5, N5C4a, C2N3, N3C4	(1375)
1573 (0.2)	δ CH$_3$(C^I,C^{II}); ν C6C5a, C9aN10, C5aN5, C2N3, C2N1	
1570 (0.2)	δ CN3H; νC6C5a, C9aN10, C2N3, C5aN5	
1562 (0.0)	δ CH$_3$(C^I,C^{II}); ν N10C10a. C4C4a, C2N1, C4N3	
1509 (10.6)	ν C4C4a, C4N3, N3C2, C2N1, C4aC10a, C9aN10, C6C5a	
1470 (3.8)	ν C9aN10, N10C(CH$_3$), C4aC10a, C5aN5, C4aC4	

Table S4. Computed CIS/6-31G(d) harmonic normal modes and frequencies of the N(5)-protonated lumiflavin cation in the first triplet state

Comput. frq. cm^{-1}, (IR intensity)	Normal mode major components, ν – stretch, δ – bend
2130 (80.3)	ν C5aN5, N5C4a, C4aC10a, C10aN1, C9aN10, C4aC4
2035 (42.8)	ν C(2)=O, C5aN5, N5C4a
1977 (19.0)	ν C(4)=O, N5C4a, C10aN1
1781 (5.4)	ν C6C7, C8C9, C9C9a, C9aN10, C10aN1, C5aN5, N5C4a, C4aC4
1747 (11.4)	δ CN5H; ν C6C7, C7C8, C9aC5a, N10C10a, N5C4a, C10aN1
1722 (4.5)	ν C8C9, C9C9a, C10aN1, C5aN5, C4aC4, C4N3
1660 (2.5)	δ CN5H, CH$_3$(N10,C^{I},C^{II}); ν C7C8, C9aN10, C5aN5, C4aC10a
1654 (0.4)	δ CH$_3$(N10)
1648 (0.6)	δ CH$_3$(N10,C^{I},C^{II}); ν C7C8, C10aN10
1635 (0.3)	δ CN5H, CH$_3$(N10,C^{I},C^{II}); ν C6C5a, C5aN5, C4aC10a, C9aN10
1628 (0.7)	δ CH$_3$(C^{I},C^{II})
1616 (1.8)	δ CH$_3$(C^{I},C^{II}); ν C9C9a, C9aN10, C6C5a, C5aN5, N5C4a, N10C10a, C10aN1
1612 (1.2)	δ CN5H, CH$_3$(N10,C^{I}); ν C9aN10, N10C10a, C10aC4a, C5aN5
1612 (0.0)	δ CH$_3$(C^{I},C^{II})
1602 (3.1)	δ CH$_3$(C^{I},C^{II}), HCC; ν C7C8, C9C9a, C6C5a
1573 (1.5)	δ CN3H; ν C9aN10, N10C10a, C5aN5, N5C4a, C4aC4, C2N3
1570 (0.0)	δ CN3H, CH$_3$(C^{I},C^{II})
1563 (2.1)	δ CN3H, CH$_3$(N10,C^{II}); ν C9aN10, N10C(CH$_3$), C10aN1, C4aC4, C4N3
1560 (1.8)	δ CH$_3$(N10,C^{I},C^{II}); ν C9aN10, N10C(CH$_3$), C6C5a, C4aC4, C4N3
1544 (0.0)	δ CN5H; ν C8C9, C7C6, C9aN10, C5aN5, C10aN1, C4aC4, C4C3