

Photoinduced Electron Transfer of *N*-(3- and 4-Diarylamino)phenyl]-1,8-Naphthalimide Dyads: Orbital-orthogonal Approach in a Short-linked D-A System

Seiichiro Takahashi,^a Koichi Nozaki,*^b Masatoshi Kozaki,^a Shuichi Suzuki,^a Kazutoshi Keyaki,^b Akio Ichimura,^a Toshio Matsushita,^a and Keiji Okada*^a

^a Department of Chemistry, Graduate School of Science, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

^b Department of Chemistry, Graduate School of Science and Engineering, University of Toyama, 3190 Gofuku, Toyama 930-8555, Japan

Supplementary Data

Content

1. Synthetic procedures and compound data for **4m**, **4p**, **5m**, and **5p**. (pp. 2-5)
2. Absorption spectra of **1-5** in toluene. Figures S1-S5 (pp. 6-7)
3. Fluorescence spectra of **1-3**, **5**, and model compounds. Figures S6-S15 (pp. 8-9)
4. Phosphorescence spectra of model compounds, **1-3**, and **5**. Figures S16-S21 (p. 10)
5. Spectral change during the electrochemical reduction of **NI-Ph** and oxidation of reference compounds. Figures S22-S26 (p. 11)
6. Laser photolysis of **1-5** in toluene or dioxane. Figures S27-S37 (pp. 12-14)
7. Laser photolysis of **1-5** in DMF. Figures S38-S41 (p. 15)
8. TD-DFT calculation for **1-5**. Figures 40 (pp. 16-20)

1. Synthesis of Materials and Compound data

Syntheses of Materials. The syntheses of **3m** and **3p** are described in the main text. The synthetic procedures of **4m**, **4p**, **5m**, and **5p** are described here. Compounds, **1m**, **1p**, **2m**, and **2p** were prepared in a similar manner as **3m** and **3p**.

N-[3-(diphenyamino)phenyl]-1,8-naphthalimide (1m). A yellow powder from toluene (51% yield), mp: 251 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.62 (d, *J* = 7.8 Hz, 2H), 8.25 (d, *J* = 7.8 Hz, 2H), 7.77 (t, *J* = 7.8 Hz, 2H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.36-7.17 (m, 8H), 7.14 (d, *J* = 8.0 Hz, 1H), 7.03-7.00 (m, 3H), 6.92 (d, *J* = 8.0 Hz, 1H), IR (KBr) 1715, 1668, 1587, 1485, 1437, 1379, 1358, 1273, 1236, 1192, 779, 754, 702 cm⁻¹, High-resolution MS: found m/z 440.1524; calcd for C₃₀H₂₀N₂O₂ m/z 440.1525.

N-[4-(diphenyamino)phenyl]-1,8-naphthalimide (1p). A yellow powder from toluene (36% yield), mp: 296 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.66 (d, *J* = 7.8 Hz, 2H), 8.27 (d, *J* = 7.8 Hz, 2H), 7.80 (t, *J* = 7.8 Hz, 2H), 7.31-7.27 (m, 4H), 7.21-7.14 (m, 8H), 7.06 (t, *J* = 7.3 Hz, 2H), IR (KBr) 1705, 1666, 1624, 1585, 1508, 1493, 1371, 1358, 1315, 1294, 1283, 1236, 1188, 824, 785, 759, 698 cm⁻¹, High-resolution MS: found m/z 440.1520; calcd for C₃₀H₂₀N₂O₂ m/z 440.1525.

N-{3-[bis(4-tolyl)amino]phenyl}-1,8-naphthalimide (2m). A yellow powder from ethanol (38% yield), mp: 262 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.61 (d, *J* = 7.8 Hz, 2H), 8.24 (d, *J* = 7.8 Hz, 2H), 7.77 (t, *J* = 7.8 Hz, 2H), 7.33 (t, *J* = 7.9 Hz, 1H), 7.10-7.05 (m, 9H), 6.95 (t, *J* = 2.1 Hz, 1H), 6.84 (d, *J* = 7.9 Hz, 1H), 2.28 (s, 6H), IR (KBr) 1711, 1670, 1589, 1489, 1435, 1375, 1353, 1325, 1299, 1269, 1238, 1188, 777 cm⁻¹, MS(FAB⁺) 468 [M⁺], Anal. Calcd for C₃₂H₂₄N₂O₂: C 82.03, H 5.16, N 5.98, found: C 81.92, H 5.05, N, 5.90.

N-{4-[bis(4-tolyl)amino]phenyl}-1,8-naphthalimide (2p). A yellow powder from ethanol (38% yield), mp: 296 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.65 (d, *J* = 7.8 Hz,

2H), 8.27 (d, J = 7.8 Hz, 2H), 7.79 (t, J = 7.8 Hz, 2H), 7.15-7.10 (m, 12H), 2.32 (s, 6H), IR (KBr) 1707, 1668, 1624, 1603, 1587, 1506, 1434, 1373, 1356, 1317, 1294, 1236, 1188, 1140, 1111, 822, 781 cm^{-1} , MS(FAB $^{+}$) 468 [M $^{+}$], Anal. Calcd for C₃₂H₂₄N₂O₂: C 82.03, H 5.16, N 5.98, found: C 82.12, H 5.17, N 5.78.

N-[3-[bis(4-dimethylaminophenyl)amino]phenyl]-1,8-naphthalimide (4m). In a 50 mL two-necked flask, sodium *tert*-butoxide (249 mg, 2.59 mmol) and Pd₂(dba)₃·CHCl₃ (18 mg, 0.017 mmol), anhydrous toluene (20 mL), and a solution of P('Bu)₃ in toluene (0.152 M, 0.20 ml, 0.030 mmol) were taken and stirred under a nitrogen atmosphere. To this mixture were added *N,N*-dimethyl-1,4-phenylene diamine (116 mg, 0.852 mmol), 4-bromo-*N,N*-dimethylaniline (171 mg, 0.855 mmol). The mixture was refluxed under nitrogen for 1 hr. After cooling the reaction mixture to room temperature, *N*-(3-bromophenyl)-1,8-naphthalimide (**6m**) (300 mg, 0.852 mmol), Pd₂(dba)₃·CHCl₃ (90.0 mg, 0.0869 mmol), and a solution of P('Bu)₃ in toluene (0.152 M, 1.0 ml, 0.0152 mmol) were further added. The mixture was stirred and refluxed overnight, allowed to cool and filtered through celite. The filtrate was concentrated under reduced pressure and passed through an alumina column eluted with CH₂Cl₂-toluene to give almost pure **4m**. Recrystallization from CH₂Cl₂-ether gave analytically pure sample (289 mg, 64%). **4m**: a yellow powder from dichloromethane-ether, mp 283 °C, ¹H NMR (400 MHz, pyridine-d₅) δ 8.62 (dd, J = 7.3 Hz, 1.0 Hz, 2H), 8.21 (dd, J = 8.3, 1.0 Hz, 2H), 7.67 (t, J = 7.6 Hz, 2H), 7.43 (t, J = 8.1 Hz, 1H), 7.38 (t-like s, 1H), 7.28 (d-like, J = 8.8 Hz, 4H), 7.14 (dd-like m, 2H), 6.73 (d-like, J = 8.8 Hz, 4H), 2.71 (s, 12H); IR (KBr) 1711, 1672, 1587, 1514, 1485, 1445, 1373, 1352, 1329, 1298, 1263, 1238, 1186, 1163, 1128, 947, 849, 818, 777 cm^{-1} , MS(FAB $^{+}$) 526 [M $^{+}$], Anal. Calcd for C₃₄H₃₀N₄O₂: C 77.54, H 5.47, N 10.64, found: C 77.41, H 5.68, N 10.56.

N-[3-[bis(4-dimethylaminophenyl)amino]phenyl]-1,8-naphthalimide (4p). In a 100 mL two-necked flask, sodium *tert*-butoxide (819 mg, 8.52 mmol) and Pd₂(dba)₃·CHCl₃ (61 mg, 0.059 mmol), anhydrous toluene (70 mL), and a solution of

$\text{P}(\text{'Bu})_3$ in toluene (0.100 M, 1.0 ml, 0.10 mmol) were taken and stirred under a nitrogen atmosphere. To this mixture were added *N,N*-dimethyl-1,4-phenylene diamine (391 mg, 2.87 mmol), 4-bromo-*N,N*-dimethylaniline (569 mg, 2.84 mmol). The mixture was refluxed under nitrogen for 1 hr. After cooling to room temperature, *N*-(4-bromophenyl)-1,8-naphthalimide (**6p**) (1.00 g, 2.84 mmol), $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (302 mg, 0.292 mmol), and a solution of $\text{P}(\text{'Bu})_3$ in toluene (0.100 M, 5.0 ml, 0.50 mmol) were added. The mixture was stirred and refluxed overnight, allowed to cool and filtered through celite. The filtrate was concentrated under reduced pressure and passed through an alumina column eluted with CH_2Cl_2 -toluene to give almost pure **4p**. Recrystallization from methylenechloride-ether gave analytically pure sample (390 mg, 26%). **4p**: a yellow powder from dichloromethane-ether, mp >300 °C, ^1H NMR (400 MHz, pyridine-d₅) δ 8.69 (d, J = 7.8 Hz, 2H), 8.23 (d, J = 7.8 Hz, 2H), 7.70 (t, J = 7.8 Hz, 2H), 7.50 (d, J = 8.8 Hz, 2H), 7.27-7.15 [6H involving (d, J = 8.8 Hz, 4H) and 2H overlapped with pyridine-d₅], 6.77 (d-like, J = 8.8 Hz, 4H), 2.80 (s, 12H); IR (KBr) 1707, 1668, 1605, 1585, 1441, 1373, 1352, 1356, 1323, 1306, 1286, 1236, 1188, 1138, 819, 781 cm⁻¹, HRMS(FAB⁺) calcd for $\text{C}_{34}\text{H}_{30}\text{N}_4\text{O}_2$ (M^+) 526.2369, found 526.2362.

N-[4'-[bis(4-anisyl)amino]biphenyl-3-yl]-1,8-naphthalimide (5m**).** In a 50 ml two-necked flask, **6m** (403 mg, 1.14 mmol), **7¹** (594 mg, 1.38 mmol), $\text{Pd}(\text{PPh}_3)_4$ (48 mg, 0.042 mmol), toluene (17 ml), 1,4-dioxane (14 ml), a nitrogen-purged aqueous solution of potassium carbonate (2.0 M, 3.5 ml), and a solution of $\text{P}(\text{'Bu})_3$ in toluene (0.152 M, 0.55 ml, 0.0836 mmol) were taken and stirred under a nitrogen atmosphere. The mixture was refluxed overnight. After cooling, nearly a half of the mixed solvent was removed under reduced pressure. Then, the mixture was poured into water (50 ml) and extracted with CH_2Cl_2 (30 ml × 2). The organic layers were combined and dried over Na_2SO_4 . After evaporation of the solvent, the residue was passed through a silica gel column (eluent CH_2Cl_2) to give **5m** (470 mg, 71%). **5m**: a yellow powder from ethylacetate-ethanol, mp 136 °C, ^1H NMR (400 MHz, CDCl_3) δ 8.67 (d, J = 7.7 Hz, 2H), 8.28 (d, J = 7.7 Hz, 2H), 7.81 (t, J = 7.7 Hz, 2H), 7.66 (d, J = 7.9 Hz, 1H), 7.58 (t, J = 7.9 Hz, 1H), 7.48 (s, 1H), 7.43 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 7.9 Hz, 1H), 7.07 (d,

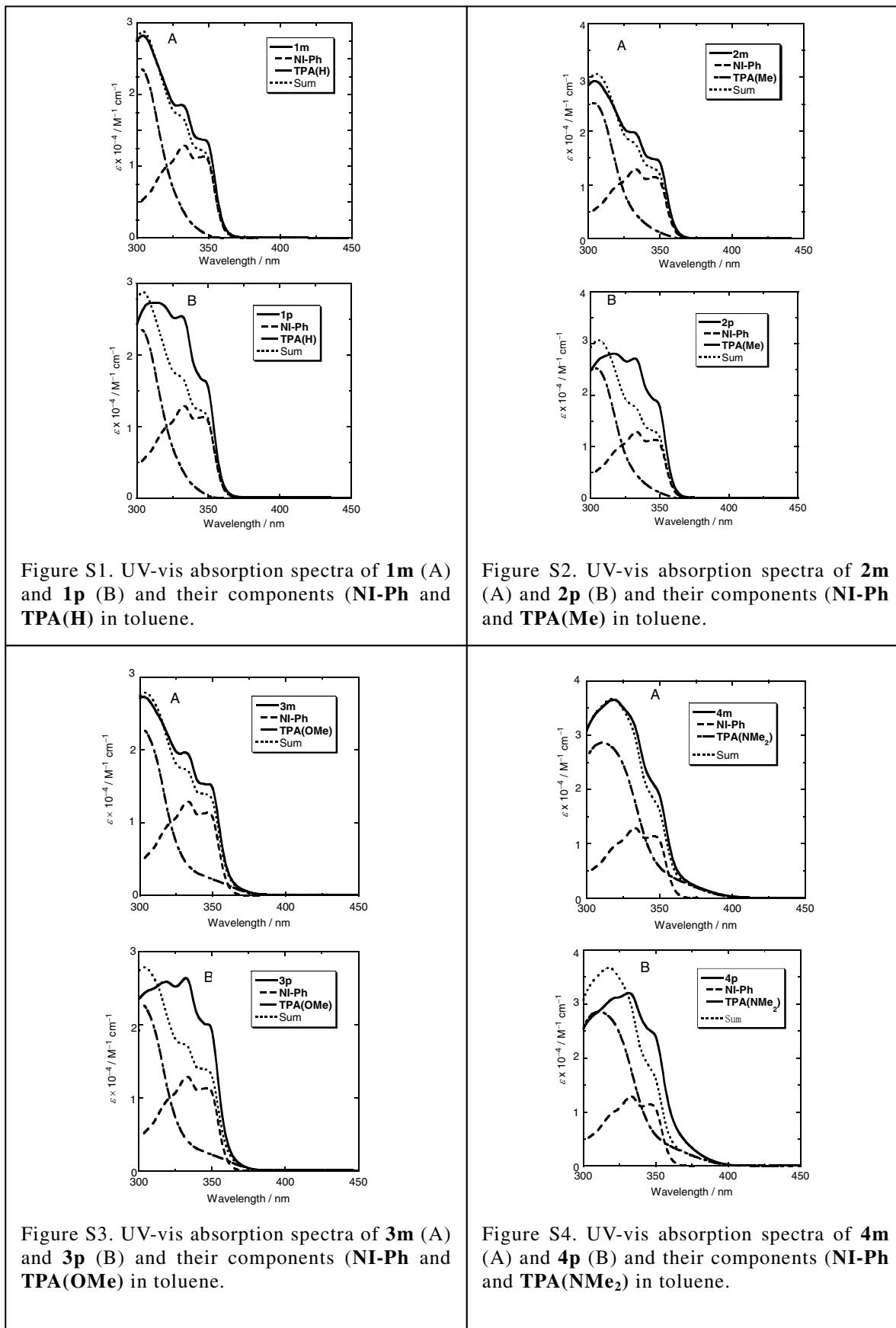
J = 8.7 Hz, 4H), 6.97 (d, *J* = 8.2 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 4H), 3.81 (s, 6H), IR (KBr) 1711, 1670, 1603, 1585, 1506, 1481, 1437, 1373, 1354, 1319, 1238, 1180, 1032, 827, 779 cm⁻¹, MS(FAB⁺) 576 [M⁺], Anal. Calcd for C₃₈H₂₈N₂O₄: C, 79.15; H, 4.89; N, 4.86, found: C, 78.96; H, 4.77; N, 4.79

N-{4'-[bis(4-anisyl)amino]biphenyl-4-yl}-1,8-naphthalimide (5p). In a 50 ml two-necked flask, **6p** (407 mg, 1.16 mmol), **7¹** (590 mg, 1.37 mmol), Pd(PPh₃)₄ (46 mg, 0.040 mmol), toluene (17 ml), 1,4-dioxane (14 ml), a nitrogen-purged aqueous solution of potassium carbonate (2.0 M, 3.5 ml), and a solution of P(^tBu)₃ in toluene (0.152 M, 0.55 ml, 0.0836 mmol) were taken and stirred under nitrogen. The mixture was refluxed overnight. After cooling, nearly a half of the mixed solvent was removed under reduced pressure, the mixture was poured into water (50 ml) and extracted with CH₂Cl₂ (30 ml × 2). The organic layers were combined and dried over Na₂SO₄. After evaporation of the solvent, the residue was passed through a silica gel column (eluent CH₂Cl₂) to give **5p** (441 mg, 66%). **5p**: a yellow powder from toluene, mp 276 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.67 (d, *J* = 7.7 Hz, 2H), 8.29 (d, *J* = 7.7 Hz, 2H), 7.81 (t, *J* = 7.7 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.9 Hz, 4H), 7.00 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.9 Hz, 4H), 3.81 (s, 6H), IR (KBr) 1707, 1668, 1605, 1585, 1504, 1494, 1458, 1437, 1375, 1352, 1238, 1032, 835, 816, 779 cm⁻¹, HRMS(FAB⁺) calcd for C₃₈H₂₈N₂O₄ (M⁺) 576.2049, found 576.2047.

Reference:

1. (a) Bushby, R. J.; McGill, D. R.; Ng, K. M.; Taylor, N. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1405-1414. (b) Amthor, S.; Lambert, C.; *J. Phys. Chem. A* **2006**, *110*, 1177-1189.

2. Absorption Spectra of **1-5** in toluene.



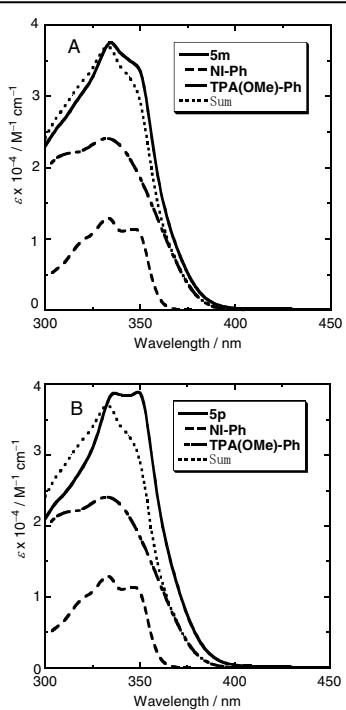


Figure S5. UV-vis absorption spectra of **5m** (A) and **5p** (B) and their components (**Ni-Ph** and **TPA(OMe)-Ph** in toluene.

3. Fluorescence spectra of **1-3**, **5**, and model compounds

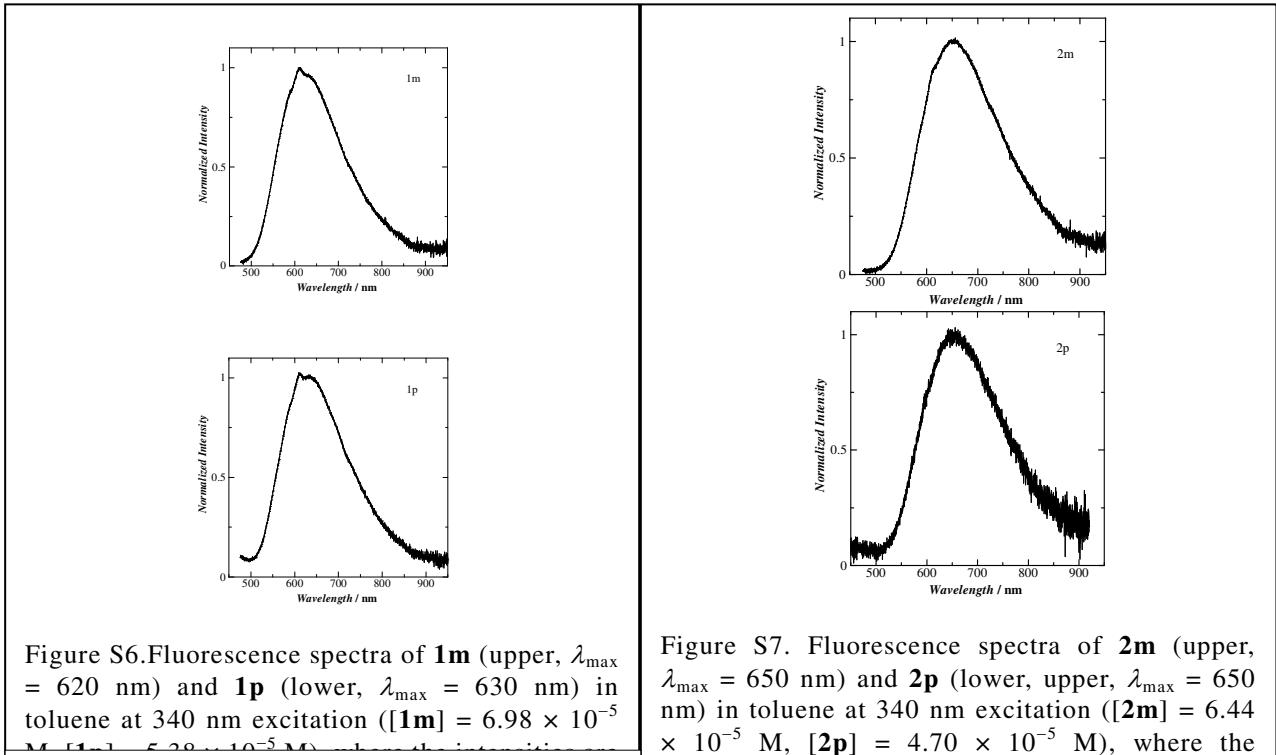


Figure S6. Fluorescence spectra of **1m** (upper, $\lambda_{\max} = 620 \text{ nm}$) and **1p** (lower, $\lambda_{\max} = 630 \text{ nm}$) in toluene at 340 nm excitation ($[1\mathbf{m}] = 6.98 \times 10^{-5} \text{ M}$, $[1\mathbf{p}] = 4.70 \times 10^{-5} \text{ M}$), where the intensities are normalized by the peak intensity.

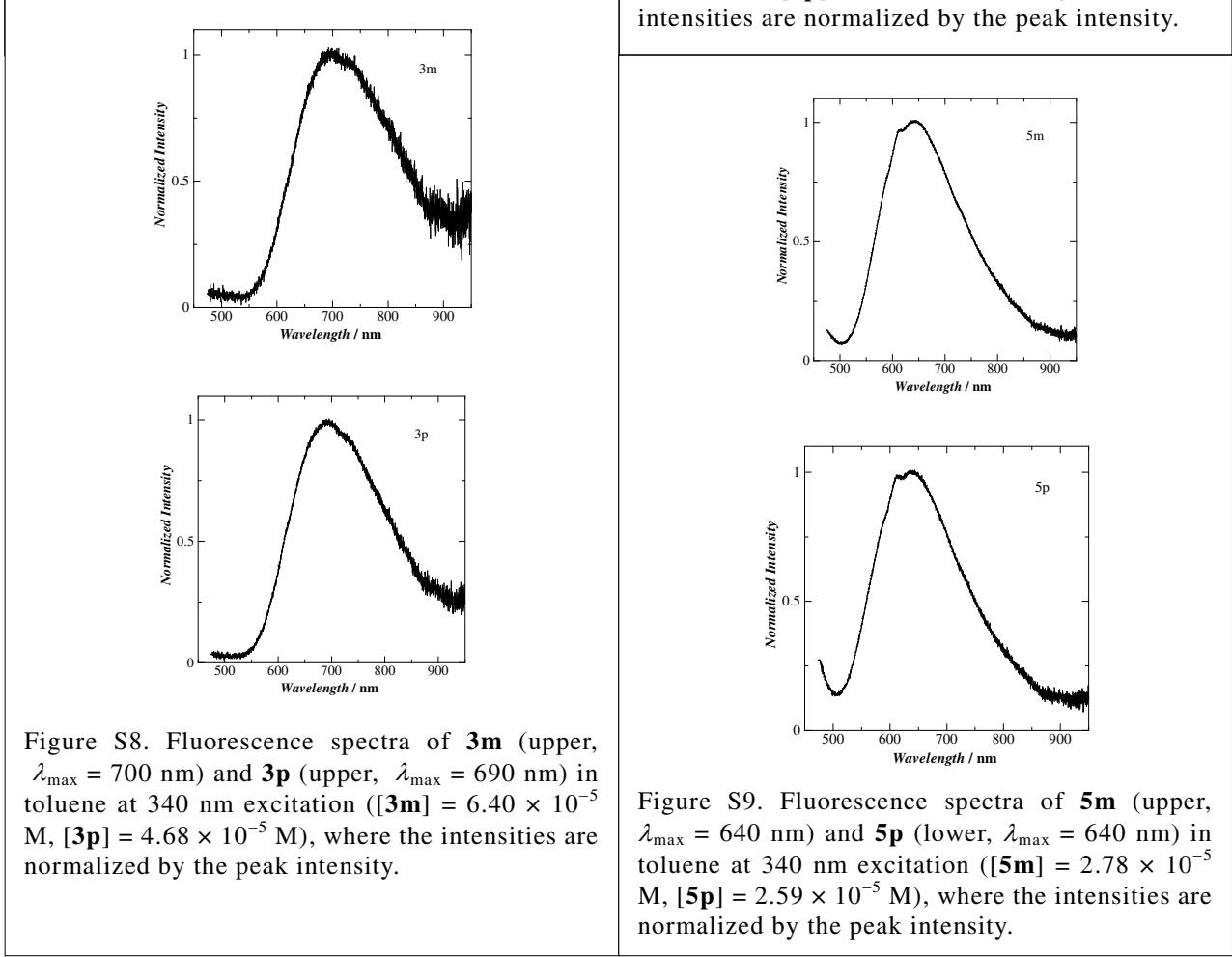


Figure S7. Fluorescence spectra of **2m** (upper, $\lambda_{\max} = 650 \text{ nm}$) and **2p** (lower, upper, $\lambda_{\max} = 650 \text{ nm}$) in toluene at 340 nm excitation ($[2\mathbf{m}] = 6.44 \times 10^{-5} \text{ M}$, $[2\mathbf{p}] = 4.70 \times 10^{-5} \text{ M}$), where the intensities are normalized by the peak intensity.

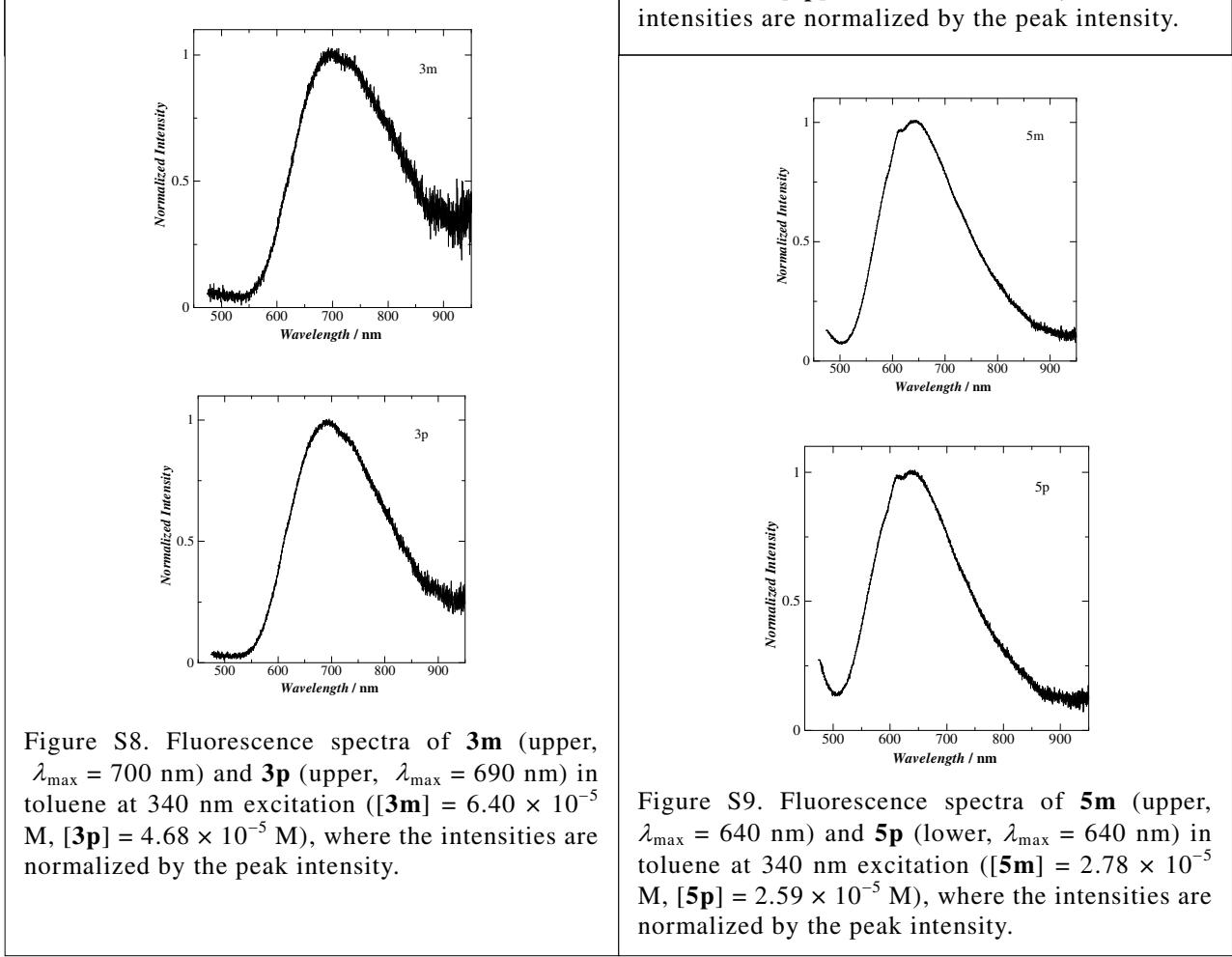


Figure S8. Fluorescence spectra of **3m** (upper, $\lambda_{\max} = 700 \text{ nm}$) and **3p** (upper, $\lambda_{\max} = 690 \text{ nm}$) in toluene at 340 nm excitation ($[3\mathbf{m}] = 6.40 \times 10^{-5} \text{ M}$, $[3\mathbf{p}] = 4.68 \times 10^{-5} \text{ M}$), where the intensities are normalized by the peak intensity.

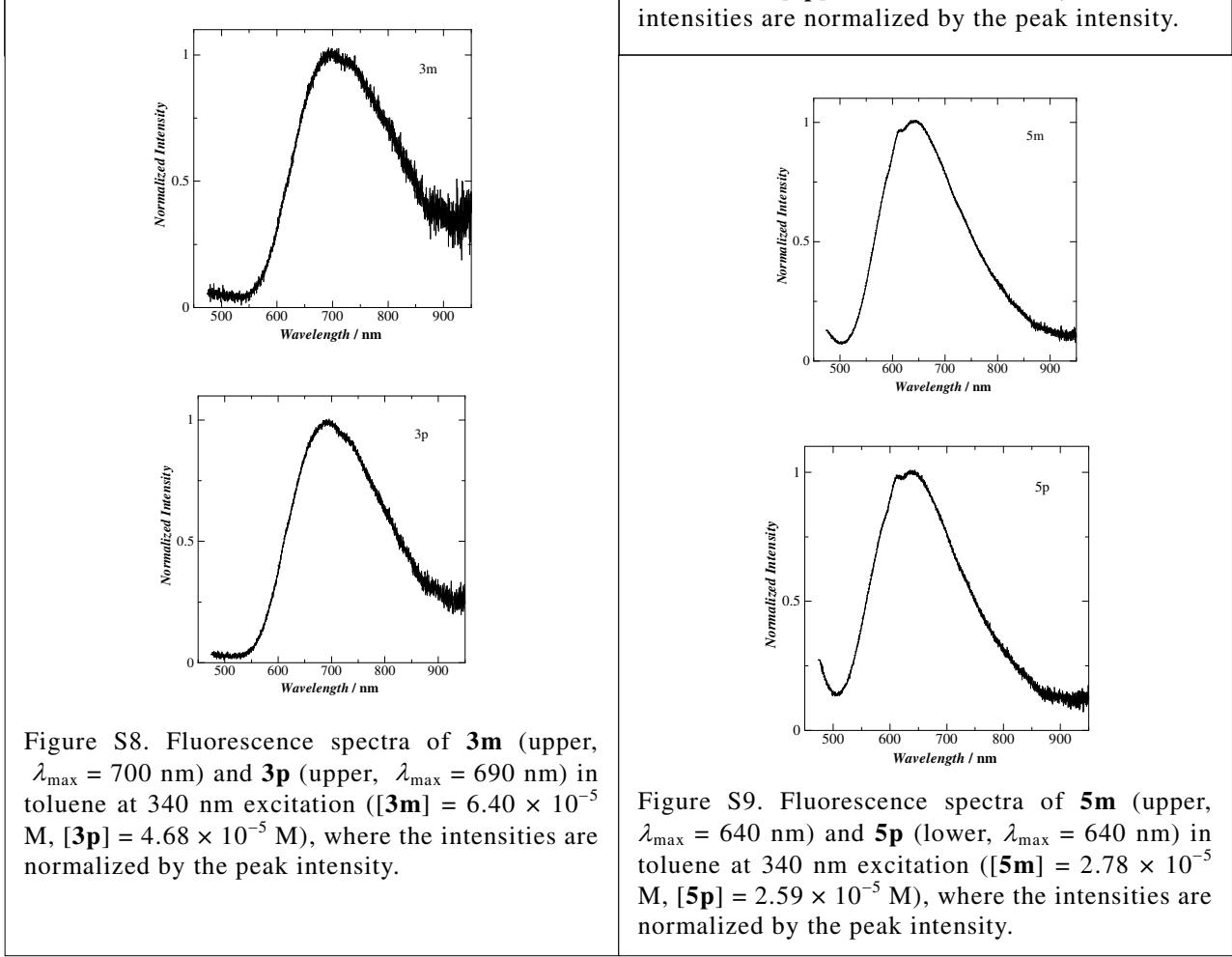


Figure S9. Fluorescence spectra of **5m** (upper, $\lambda_{\max} = 640 \text{ nm}$) and **5p** (lower, $\lambda_{\max} = 640 \text{ nm}$) in toluene at 340 nm excitation ($[5\mathbf{m}] = 2.78 \times 10^{-5} \text{ M}$, $[5\mathbf{p}] = 2.59 \times 10^{-5} \text{ M}$), where the intensities are normalized by the peak intensity.

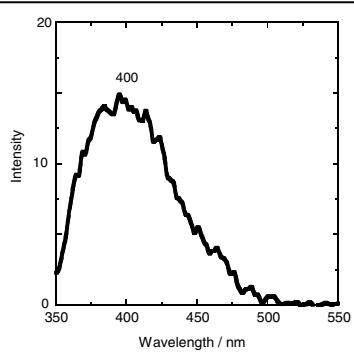


Figure S10. Fluorescence spectra of **NIPh** in toluene at 310 nm excitation ($[NIPh] = 5.37 \times 10^{-5}$ M, where the intensities are normalized by the absorbance of 310 nm.

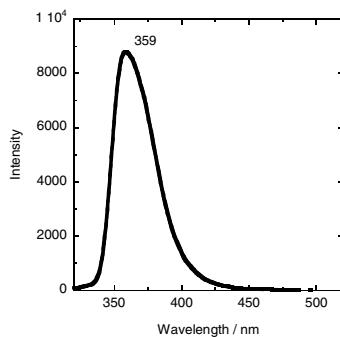


Figure S11. Fluorescence spectra of **TPA(H)** in toluene at 300 nm excitation ($[TPA(H)] = 4.05 \times 10^{-6}$ M, where the intensities are normalized by the absorbance of 300 nm.

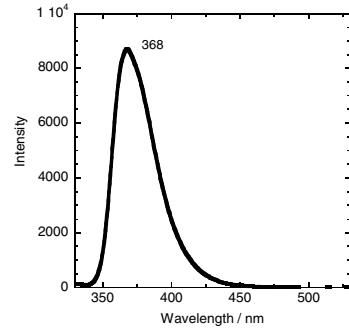


Figure S12. Fluorescence spectra of **TPA(Me)** in toluene at 300 nm excitation ($[TPA(Me)] = 3.40 \times 10^{-6}$ M, where the intensities are normalized by the absorbance of 300 nm.

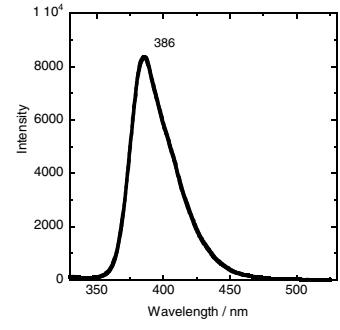


Figure S13. Fluorescence spectra of **TPA(OMe)** in toluene at 300 nm excitation ($[TPA(OMe)] = 3.77 \times 10^{-6}$ M, where the intensities are normalized by the absorbance of 300 nm.

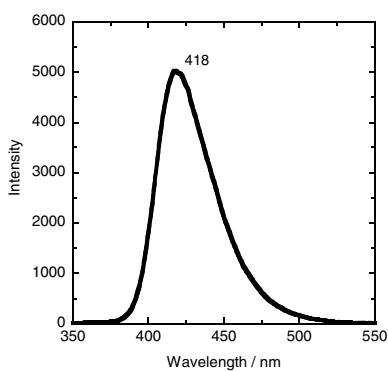


Figure S14. Fluorescence spectra of **TPA(NMe₂)** in toluene at 300 nm excitation ($[TPA(NMe_2)] = 3.07 \times 10^{-6}$ M, where the intensities are normalized by the absorbance of 300 nm.

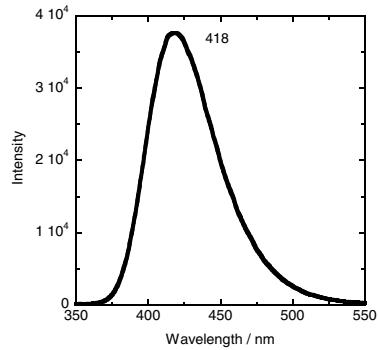
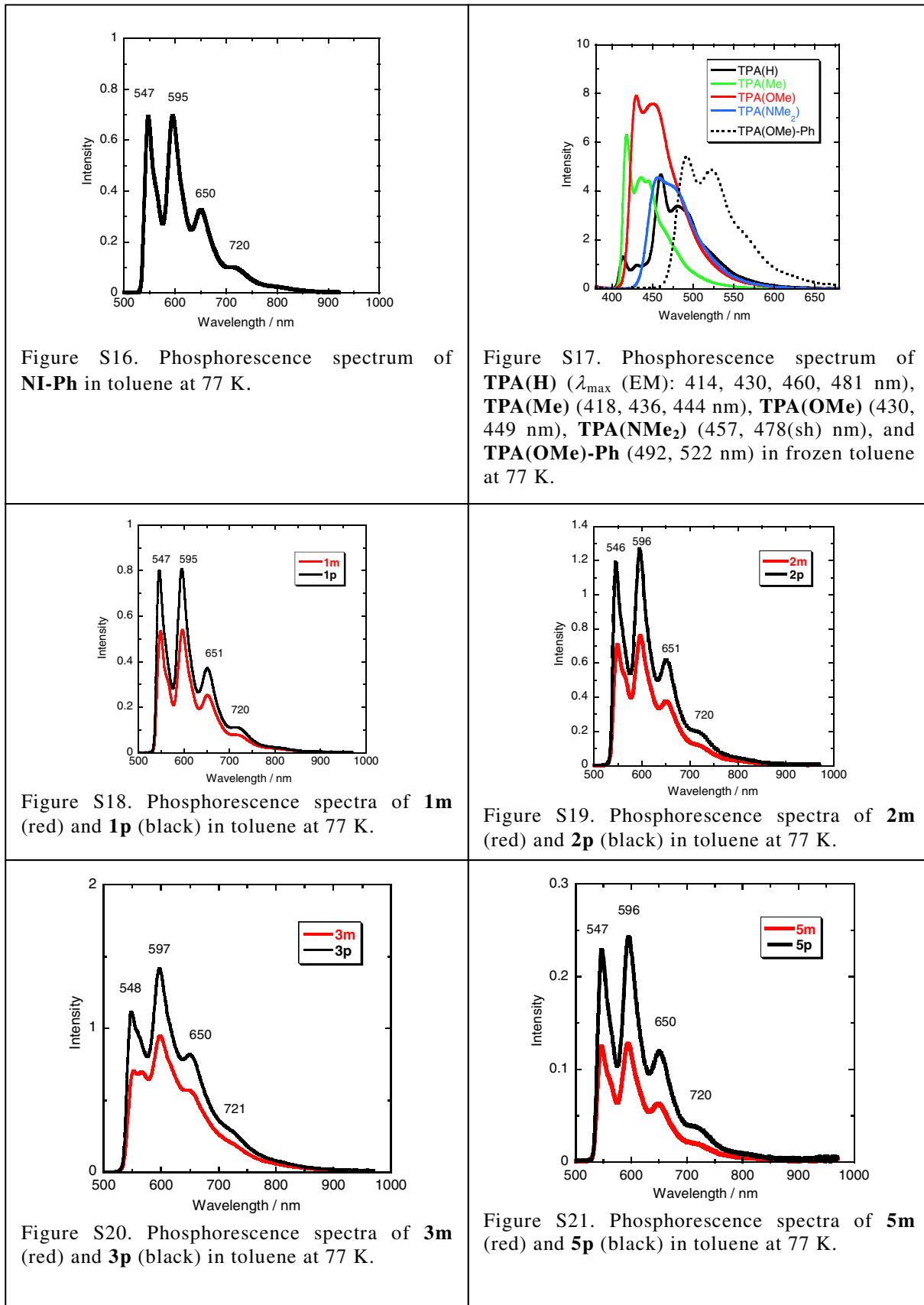


Figure S15. Fluorescence spectra of **TPA(OMe)-Ph** in toluene at 300 nm excitation ($[TPA(OMe)-Ph] = 8.35 \times 10^{-7}$ M, where the intensities are normalized by the absorbance of 300 nm.

4. Phosphorescence Spectra of model compounds, **1-3**, and **5**



5. Spectral change during the electrochemical reduction of **NI-Ph** and oxidation of reference compounds

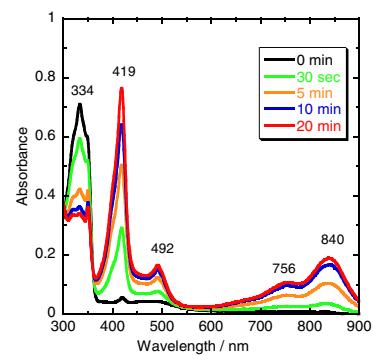


Figure S22. Spectral change during electrochemical reduction ($E_{\text{applied}} = -2.00 \text{ V}$) of **NI-Ph** in DMF ($[\text{NI-Ph}] = 5.47 \times 10^{-4} \text{ M}$).

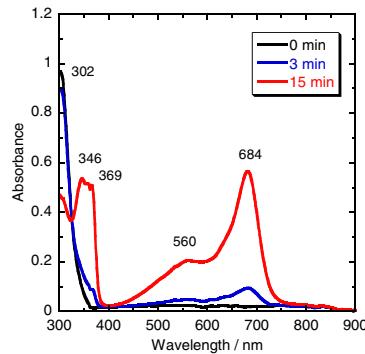


Figure S23. Spectral Change during electrochemical oxidation ($E_{\text{applied}} = +0.60 \text{ V}$) of **TPA(Me)** in CH_2Cl_2 ($[\text{TPA(Me)}] = 3.94 \times 10^{-4} \text{ M}$).

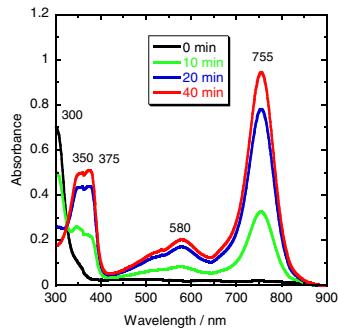


Figure S24. Spectral Change during electrochemical oxidation ($E_{\text{applied}} = +0.42 \text{ V}$) of **TPA(OMe)** in CH_2Cl_2 ($[\text{TPA(OMe)}] = 3.80 \times 10^{-4} \text{ M}$).

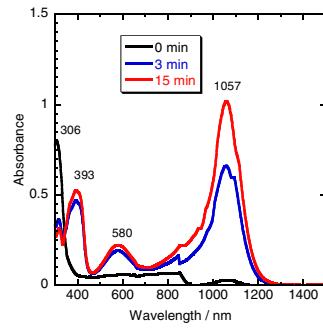


Figure S25. Spectral Change during electrochemical oxidation ($E_{\text{applied}} = +0.00 \text{ V}$) of **TPA(NMe₂)** in CH_2Cl_2 ($[\text{TPA(NMe}_2\text{)}] = 3.80 \times 10^{-4} \text{ M}$).

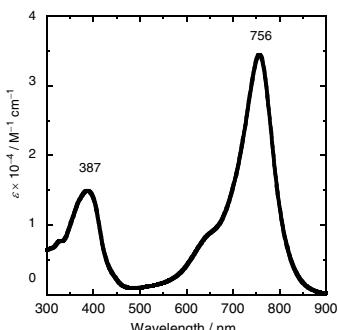
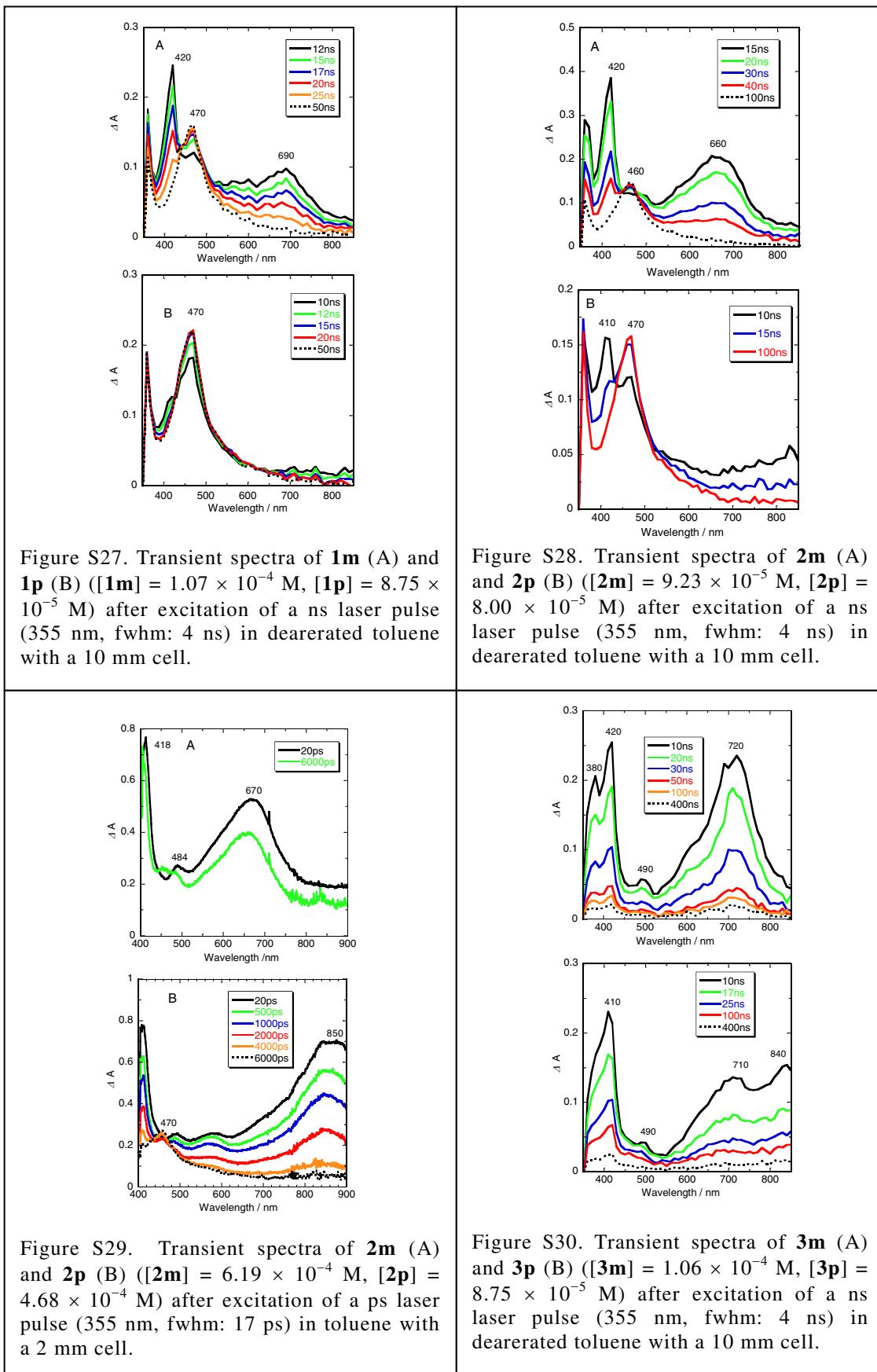


Figure S26. UV-vis spectrum of **TPA(OMe)-Ph** radical cation in CH_2Cl_2 ($[\text{TPA(OMe)-Ph}^+] = 1.52 \times 10^{-4} \text{ M}$ with a 2 mm cell).

6. Lase photolysis of **1-5** in toluene or dioxane



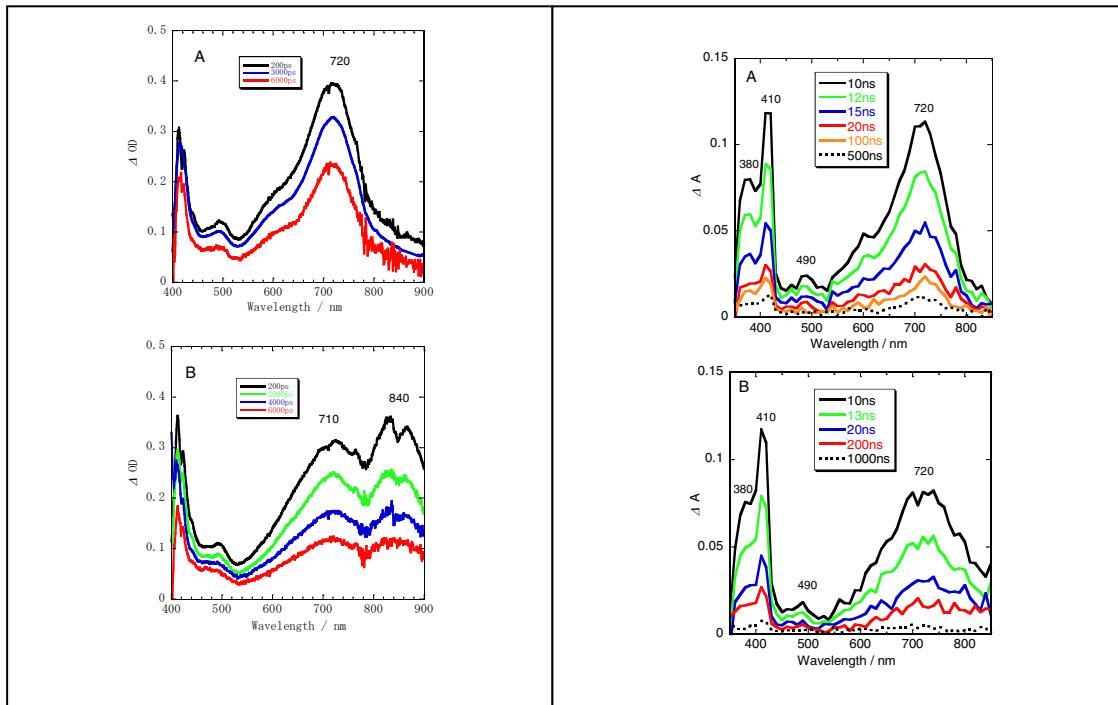


Figure S31. Transient spectra of **3m** (A) and **3p** (B) ($[3\mathbf{m}] = 5.73 \times 10^{-4}$ M, $[3\mathbf{p}] = 4.63 \times 10^{-4}$ M) after excitation of a ps laser pulse (355 nm, fwhm: 17 ps) in toluene with a 2 mm cell.

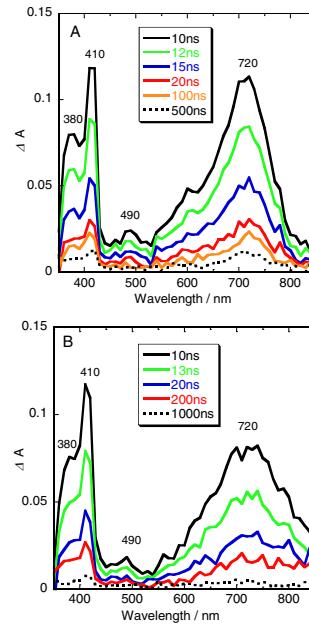


Figure S32. Transient spectra of **3m** (A) and **3p** (B) ($[3\mathbf{m}] = 1.03 \times 10^{-4}$ M, $[3\mathbf{p}] = 9.08 \times 10^{-5}$ M) after excitation of a ns laser pulse (355 nm, fwhm: 4 ns) in deaerated dioxane with a 10 mm cell.

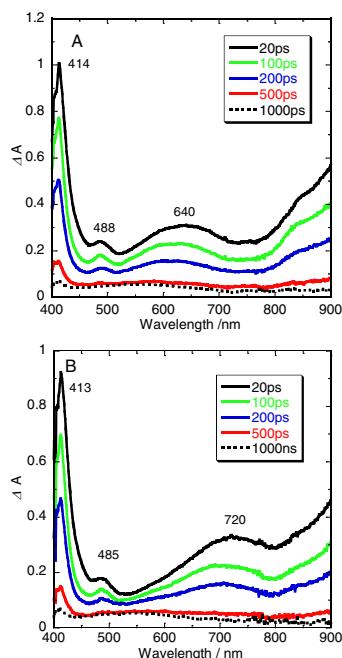


Figure S33. Transient spectra of **4m** (A) and **4p** (B) ($[4\mathbf{m}] = 3.84 \times 10^{-4}$ M, $[4\mathbf{p}] = 2.62 \times 10^{-4}$ M) after excitation of a ps laser pulse (355 nm, fwhm: 17 ps) in toluene with a 2 mm cell.

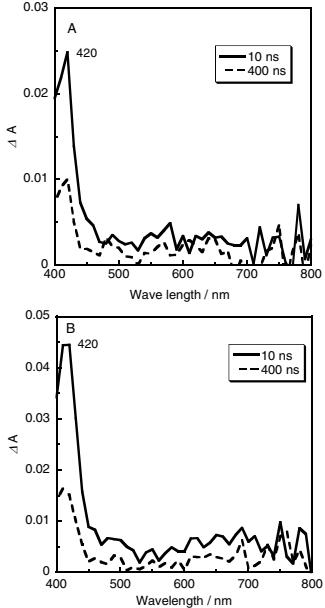


Figure S34. Transient spectra of **4m** (A) and **4p** (B) ($[4\mathbf{m}] = 8.77 \times 10^{-5}$ M, $[4\mathbf{p}] = 4.41 \times 10^{-5}$ M) after excitation of a ns laser pulse (355 nm, fwhm: 4 ns) in deaerated toluene with a 10 mm cell.

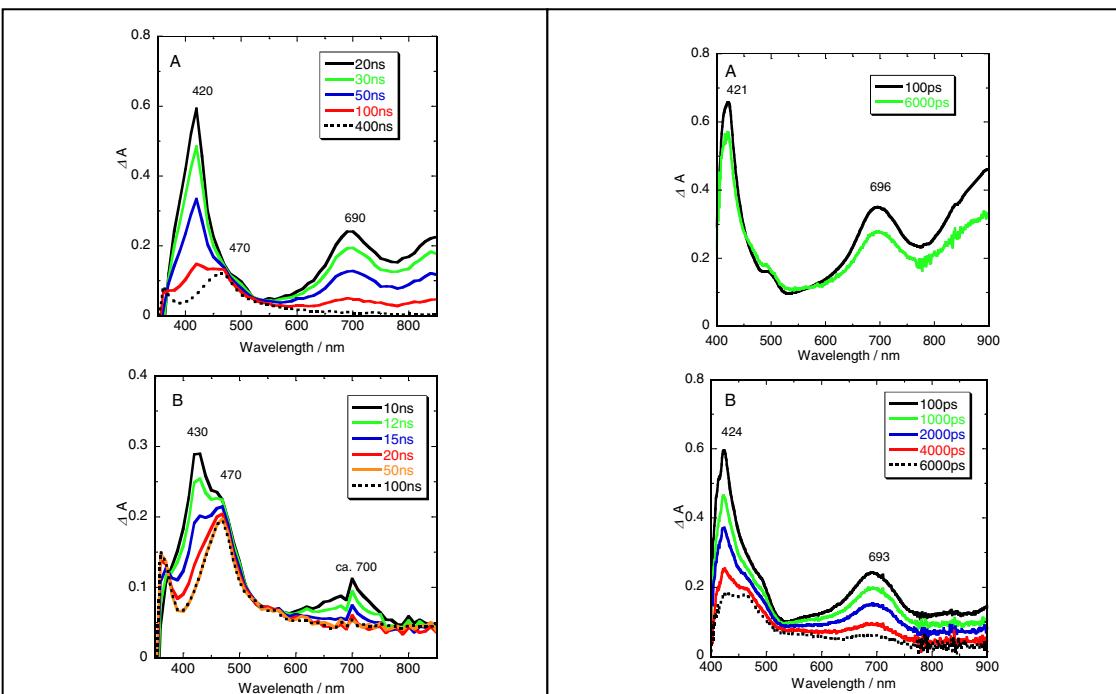


Figure S35. Transient spectra of **5m** (A) and **5p** (B) ($[5m] = 2.80 \times 10^{-5}$ M, $[5p] = 2.55 \times 10^{-5}$ M) after excitation of a ns laser pulse (355 nm, fwhm: 4 ns) in dearerated toluene with a 10 mm cell.

Figure S36. Transient spectra of **5m** (A) and **5p** (B) ($[5m] = 1.43 \times 10^{-4}$ M, $[5p] = 1.09 \times 10^{-4}$ M) after excitation of a ps laser pulse (355 nm, fwhm: 17 ps) in toluene with a 2 mm cell.

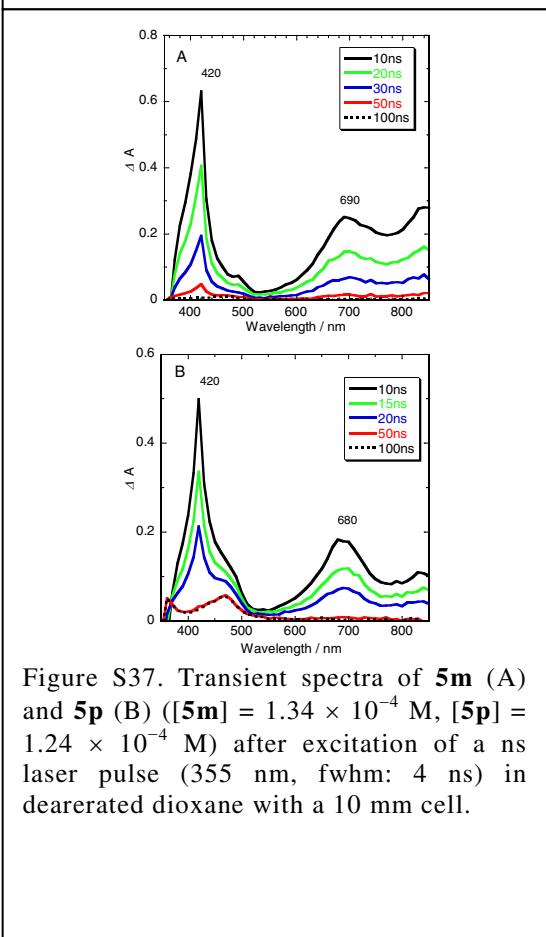
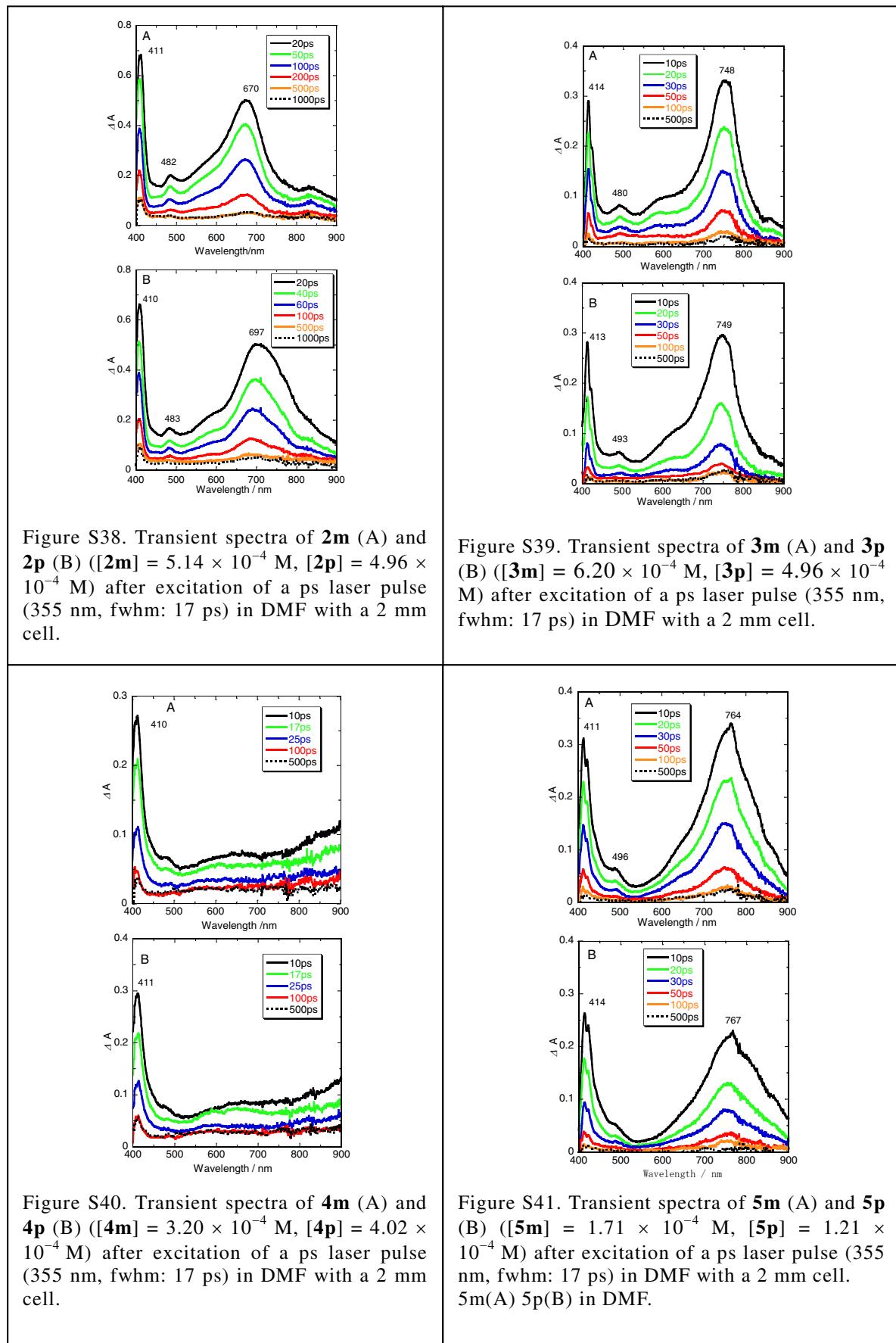


Figure S37. Transient spectra of **5m** (A) and **5p** (B) ($[5m] = 1.34 \times 10^{-4}$ M, $[5p] = 1.24 \times 10^{-4}$ M) after excitation of a ns laser pulse (355 nm, fwhm: 4 ns) in dearerated dioxane with a 10 mm cell.

7. Laser Photolysis 1-5 in DMF

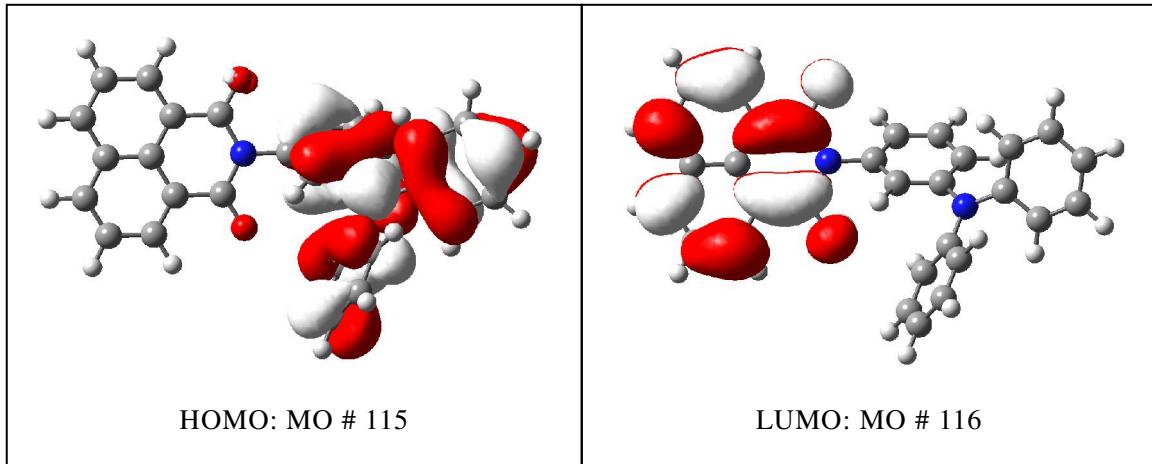


8. TD-DFT calculation of 1-5.

HOMO and LUMO and the lowest excited singlet state TD-DFT/6-31G(d):

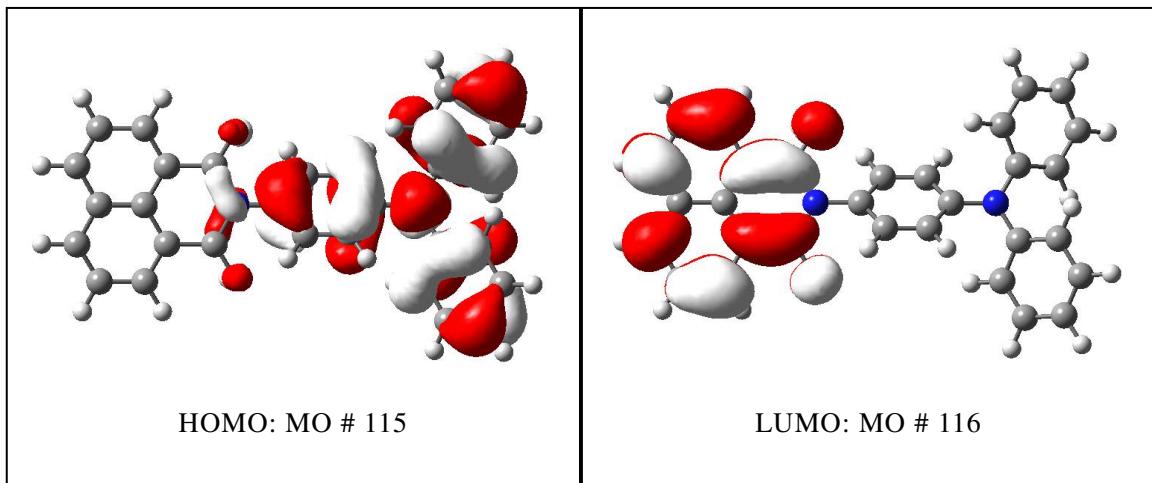
1m

Excited State 1: Singlet-A 1.8749 eV 661.30 nm f=0.0002
115 ->116 0.70563



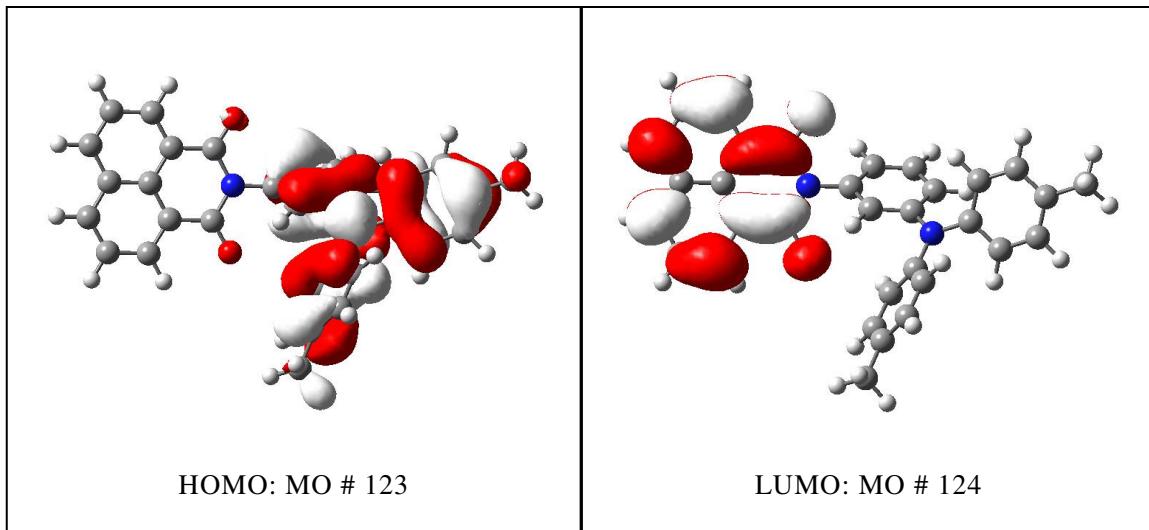
1p

Excited State 1: Singlet-A 1.9584 eV 633.08 nm f=0.0012
115 ->116 0.70229



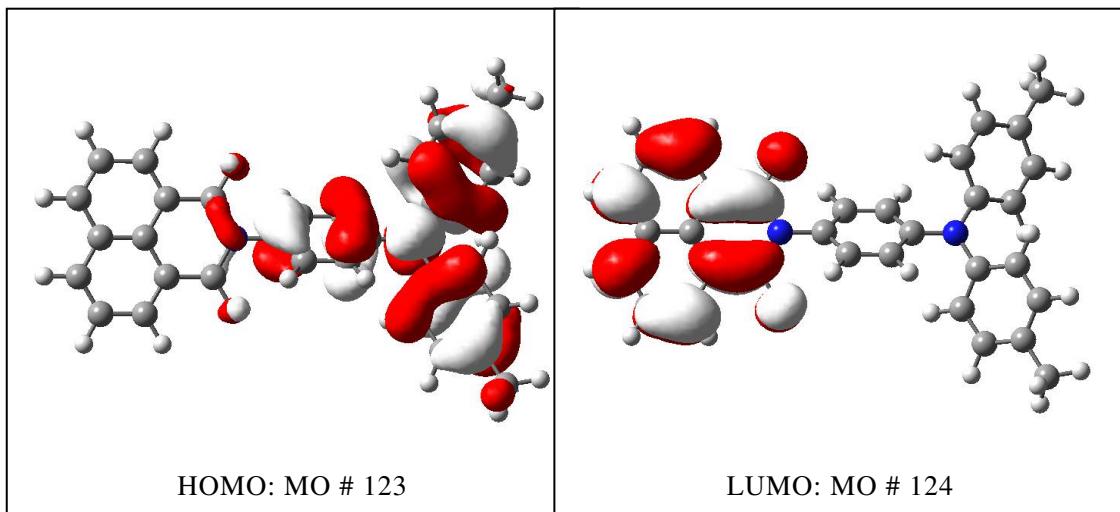
2m

Excited State 1: Singlet-A 1.7337 eV 715.13 nm f=0.0002
123 ->124 0.70574



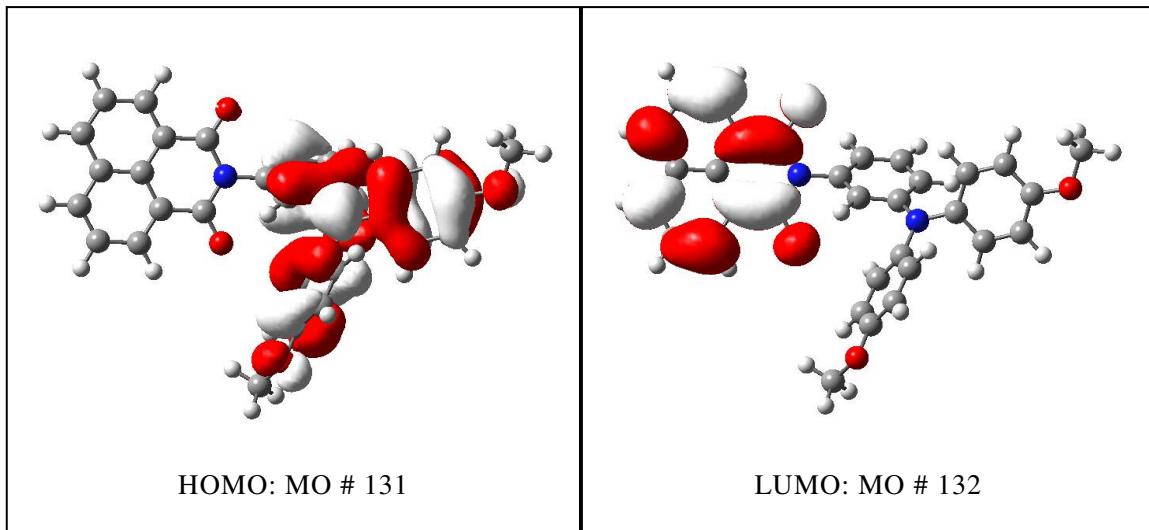
2p

Excited State 1: Singlet-A 1.8260 eV 678.98 nm f=0.0010
123 ->124 0.70258



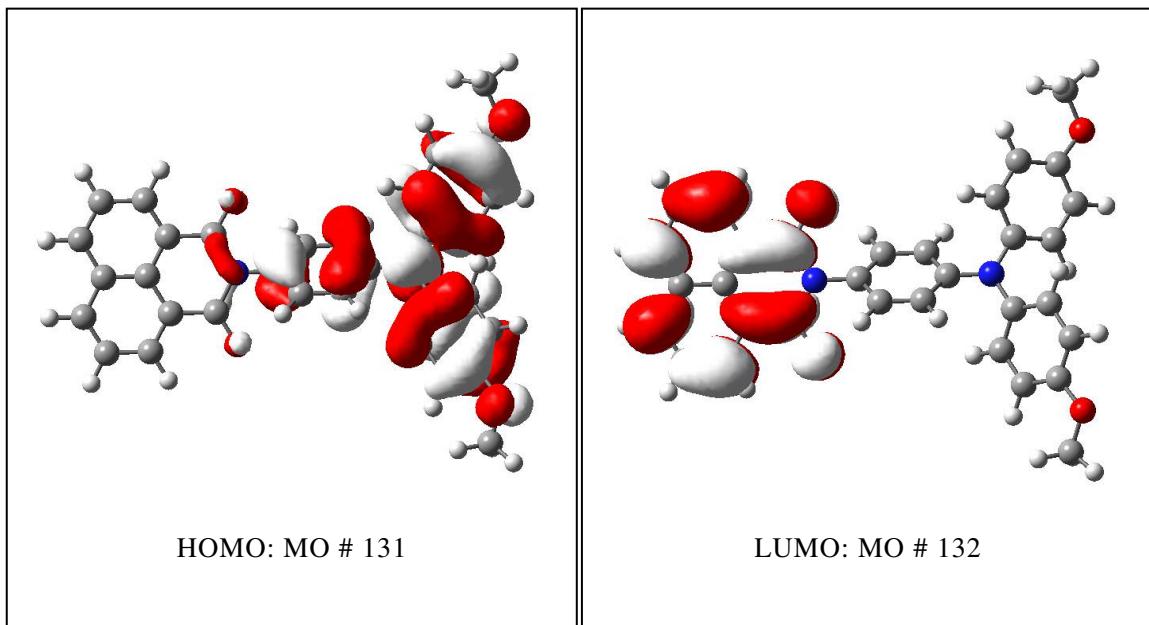
3m

Excited State 1: Singlet-A 1.5942 eV 777.71 nm f=0.0002
131 ->132 0.70578



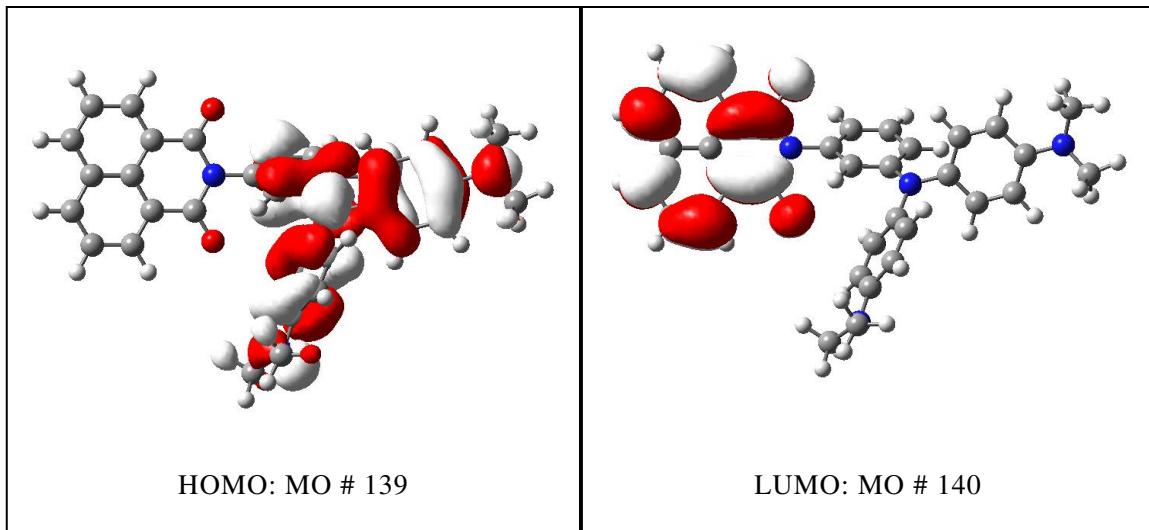
3p

Excited State 1: Singlet-B 1.6771 eV 739.28 nm f=0.0009
131 ->132 0.70266



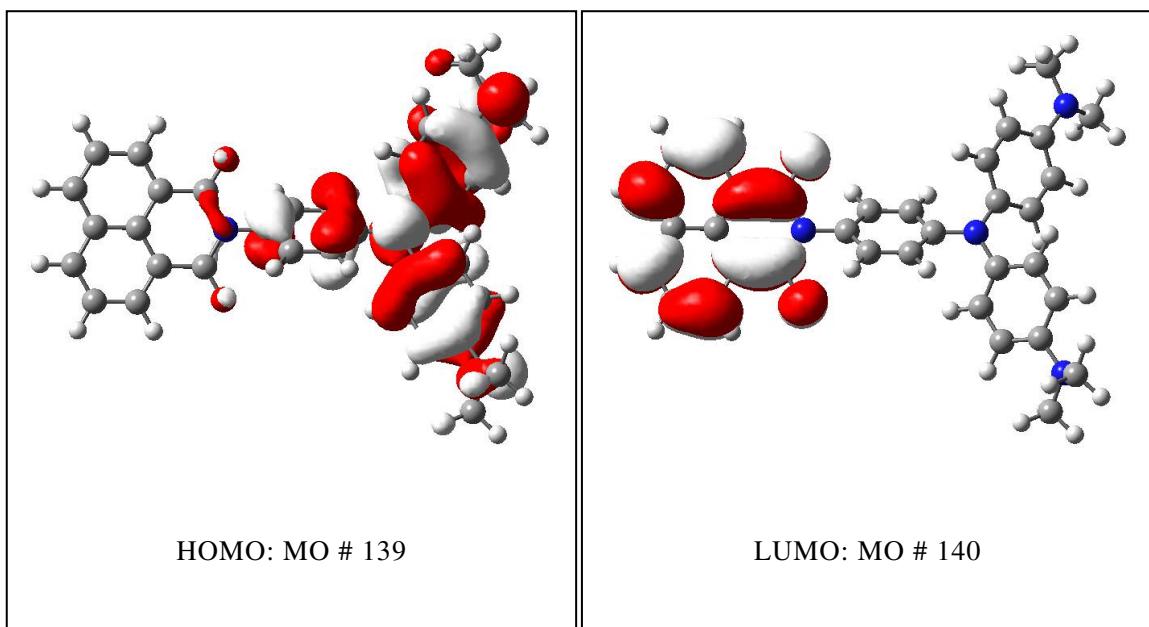
4m

Excited State 1: Singlet-A 1.3814 eV 897.50 nm f=0.0003
139 ->140 0.70563



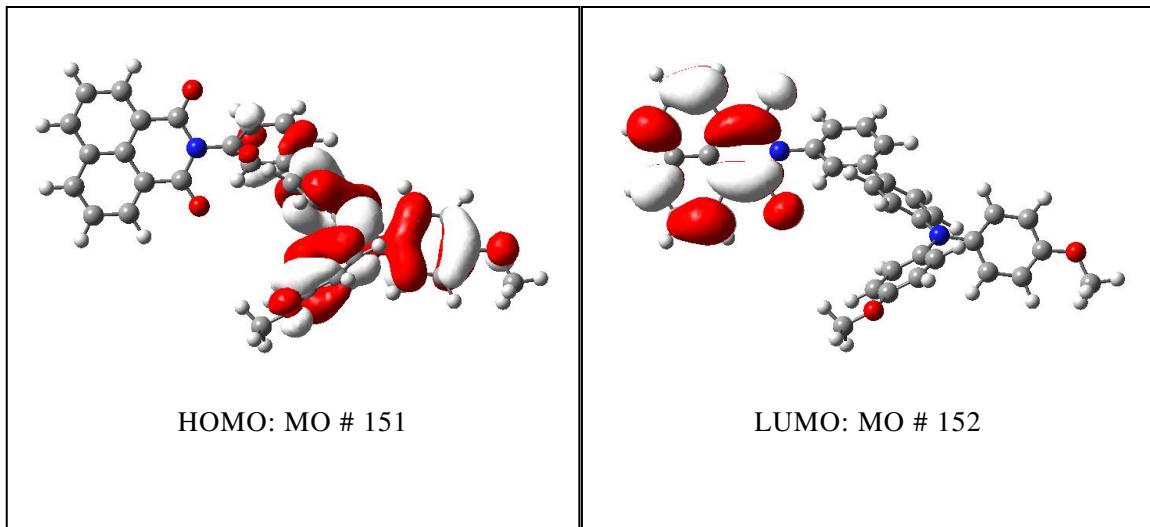
4p

Excited State 1: Singlet-A 1.5374 eV 806.47 nm f=0.0007
139 ->140 0.70284



5m

Excited State 1: Singlet-A 1.7775 eV 697.52 nm f=0.0004
151 ->152 0.70597



5p

Excited State 1: Singlet-A 1.8325 eV 676.57 nm f=0.0003
151 ->152 0.70482

