Viscosity-sensitive emission of anionic hydrogen-bonded urea-derivative–acetate-ion complexes and their aggregation-induced emission enhancement

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1. **Materials**

All chemicals were purchased from Kanto Kagaku Co., Ltd., TCI chemicals, or

Sigma-Aldrich, and used without further purification. Solvents for spectroscopic studies were of spectroscopic grade. Tetrabutylammonium acetate was purchased from Sigma-Aldrich.

1. **Syntheses**

Synthesis of 1,8-bis(4’-anilino)naphthalene1

A solution of 1,8-diiodonaphthalene (490 mg, 1.29 mmol), 4-aminophenylboronic acid pinacol ester (726 mg, 3.31 mmol), trans-(Cy2NH)2Pd(OAc)2 (195 mg, 0.332 mmol), and NaOH (239 mg, 5.98 mmol) was stirred in 9 mL of an ethanol:toluene:water (1:1:1) solution at 95 °C under N2 for 24 h. The resulting mixture was allowed to reach room temperature before undergoing celite filtration. The resulting reaction mixture was extracted with ethyl acetate three times and washed with water and brine. The separated organic layer was dried with anhydrous Na2SO4 and the solvent was removed under reduced pressure. The residue was purified via silica-gel column chromatography using an ethyl acetate:ethanol = 95:5 solution as the eluent to yield the product as a brown viscous liquid (266 mg, 0.857 mmol, 67% yield).

Synthesis of ***p*-2urea**

A solution of 1,8-bis(4’-anilino)naphthalene (195 mg, 0.628 mmol) and 4-tert-butylphenyl isocyanate (339 mg, 1.93 mmol) was stirred into 20 mL of tetrahydrofuran:N,N-dimethylformamide (3:1) at room temperature under N2 for 4 h. The resulting mixture was extracted with ethyl acetate three times and washed with water and brine. The separated organic layer was dried with anhydrous Na2SO4, and the solvent was removed under reduced pressure. The residue was collected by filtration and washed with acetone to yield ***p*-2urea** as a white powder (316 mg, 0.478 mmol, 75% yield). 1H NMR (500 MHz, DMSO-d6): δ 8.40 (d, 10 Hz, 4H), 8.00 (d, 9.5 Hz, 2H), 7.59 (t, 15.5 Hz, 2H), 7.38 (d, 8Hz, 2H), 7.29 (d, 9.0 Hz, 4H), 7.23 (d, 7 Hz 4H), 7.07 (d, 8.5 Hz,4H), 6.85 (d, 8.5 Hz, 4H), 1.24 (s,18H) ppm; 13C NMR (500 MHz, DMSO-*d*6): δ 152.54, 144.10, 139.96, 137.72, 137.22, 136.32, 135.43, 130.72, 129.81, 128.79, 128.24, 125.43, 118.23, 116.83, 34.00, 31.42 ppm. Single crystals of *p-*2urea for single-crystal X-ray diffraction analysis were obtained by vapour diffusion of diethyl ether into a DMSO solution.

Synthesis of 1,8-bis(3’-anilino)naphthalene

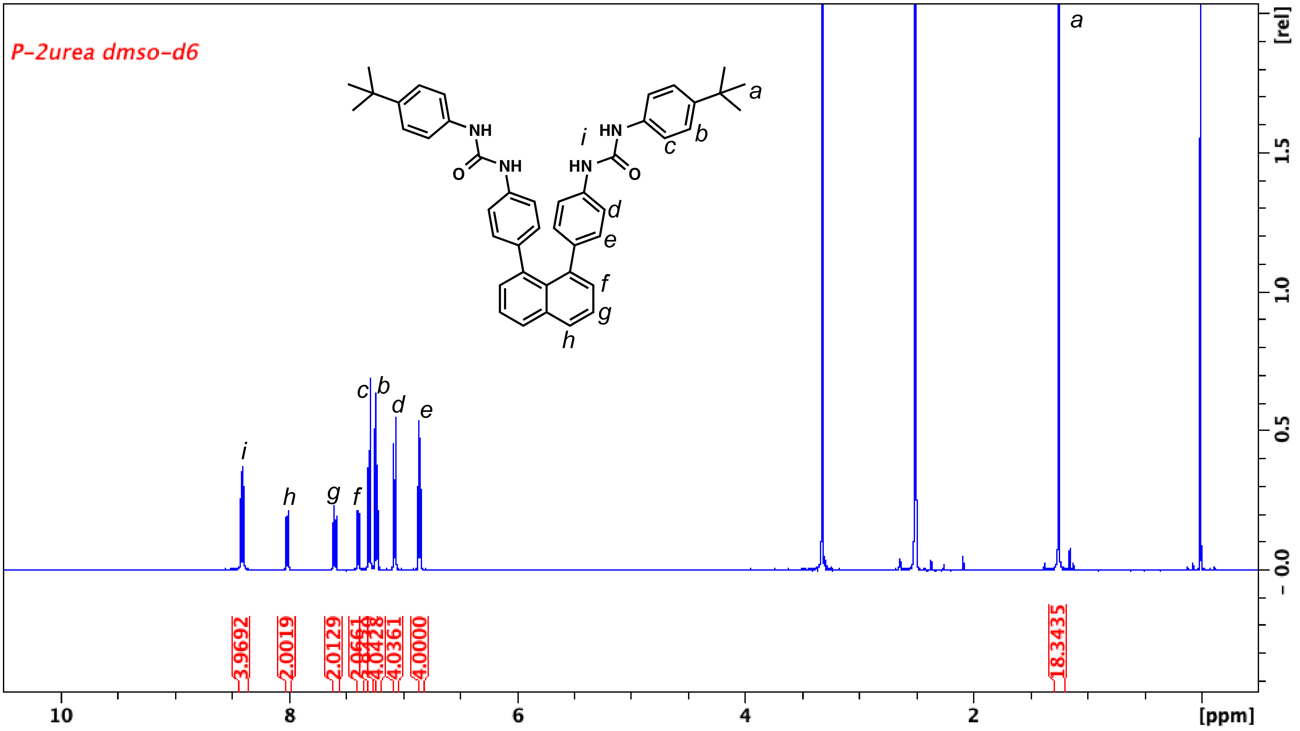
A solution of 1,8-diiodonaphthalene (490 mg, 1.29 mmol), 3-aminophenylboronic acid pinacol ester (726 mg, 3.31 mmol), trans-(Cy2NH)2Pd(OAc)2 (194 mg, 0.330 mmol), and NaOH (250 mg, 6.25 mmol) were stirred into 9 mL of an ethanol:toluene:water (1:1:1) solution at 95 °C under N2 for 24 h. The resulting mixture was allowed to reach room temperature and then underwent celite filtration. The resulting reaction mixture was extracted with ethyl acetate three times and washed with water and brine. The separated organic layer was dried with anhydrous Na2SO4 and the solvent was removed under reduced pressure. The residue was purified via silica-gel column chromatography using an ethyl acetate:ethanol = 95:5 solution as the eluent to yield the product as a brown viscous liquid (270 mg, 0.869 mmol, 67% yield). This material was used in the following step without further purification.

Synthesis of ***m*-2urea**

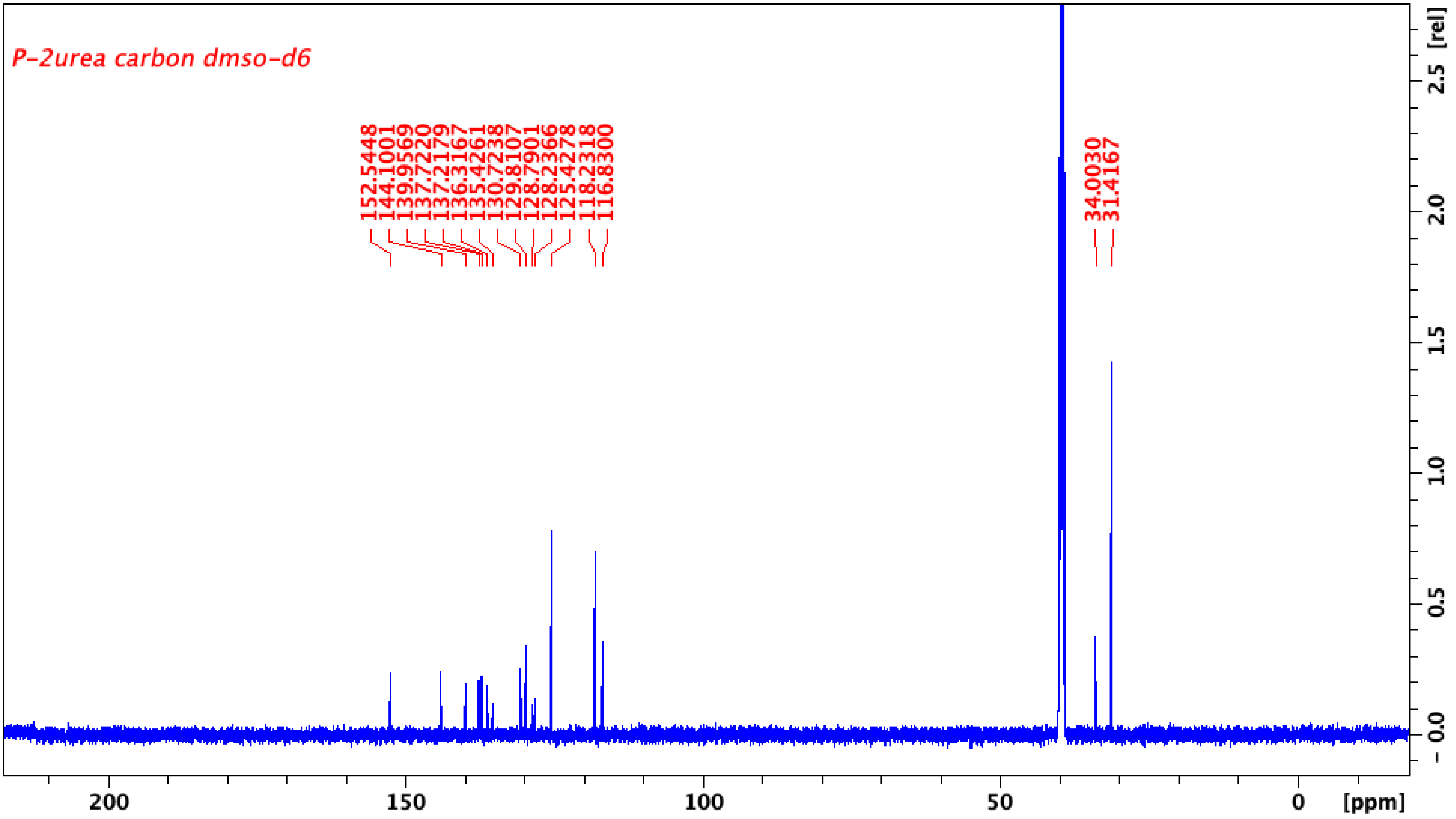
A solution of 1,8-bis(3’-anilino)naphthalene (234 mg, 0.754 mmol) and 4-tert-butylphenyl isocyanate (253 mg, 1.45 mmol) was stirred into 7.2 mL of dehydrated tetrahydrofuran at 76 °C under N2 overnight. After the solvent was removed under reduced pressure, the residue was collected by filtration and washed with acetone to yield ***m*-2urea** as a white powder (290 mg, 0.438 mmol, 58% yield). 1H NMR (500 MHz, DMSO-d6): δ8.46 (s, 1H), 8.31 (s, 1H), 8.22 (s, 2H), 8.06 (d, J = 8.2 Hz, 2H), 7.62 (t, J = 7.8 Hz, 2H), 7.43 (d, J = 6.9 Hz, 2H), 7.34 (d, J = 8.5 Hz, 2H), 7.27 (d, J = 8.5 Hz, 2H), 7.13-7.19 (m, 5H), 7.00-6.93 (m, 4H), 6.90 (s, 1H), 6.83 (t, J = 7.7 Hz, 1H), 6.76 (d, J = 6.7 Hz, 1H), 6.56 (d, J = 7.5 Hz, 1H), 1.25 (s, 9H), 1.23 (s, 9H) ppm; 13C NMR (500 MHz, DMSO-d6): δ152.86, 152.81, 144.45, 144.24, 143.32, 140.44, 138.90, 138.81, 137.61, 137.43, 135.59, 130.95, 130.84, 128.96, 127.98, 127.72, 125.83, 125.80, 125.59, 122.98, 122.87, 120.20, 119.70, 118.58, 118.38, 116.07, 34.34, 34.27, 31.72 ppm; HRMS (ESI) exact mass calculated for [M]+ (C44H44N4O2) requires *m*/*z* 660.3464, found *m*/*z* 660.3459.

***p*-1urea** was synthesised by following the method reported in our previous paper2.

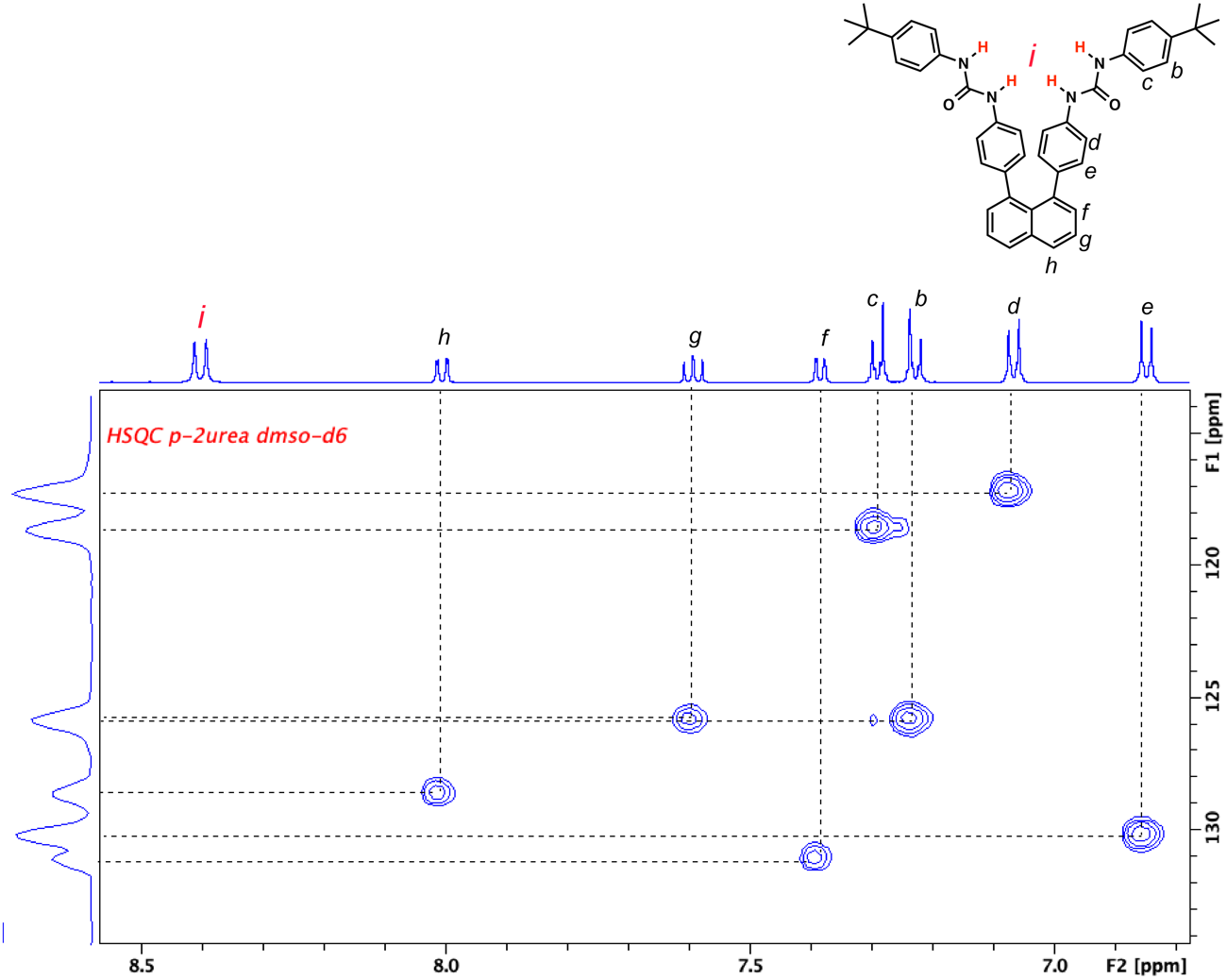
1. **Supplementary Tables and Figures**



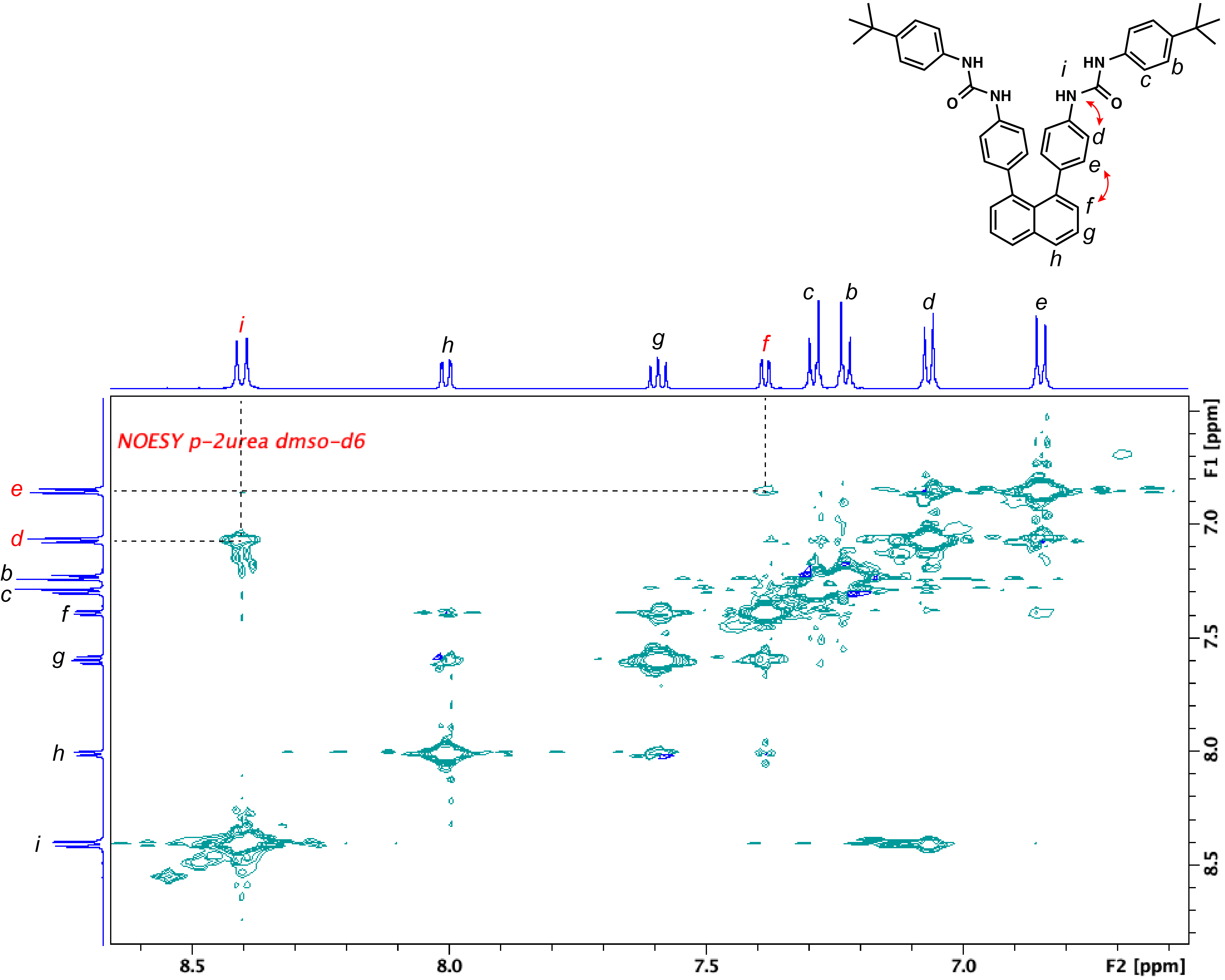
**Supplementary Figure 1.** ¹H NMR spectrum of ***p-*2urea** in DMSO-*d*6.



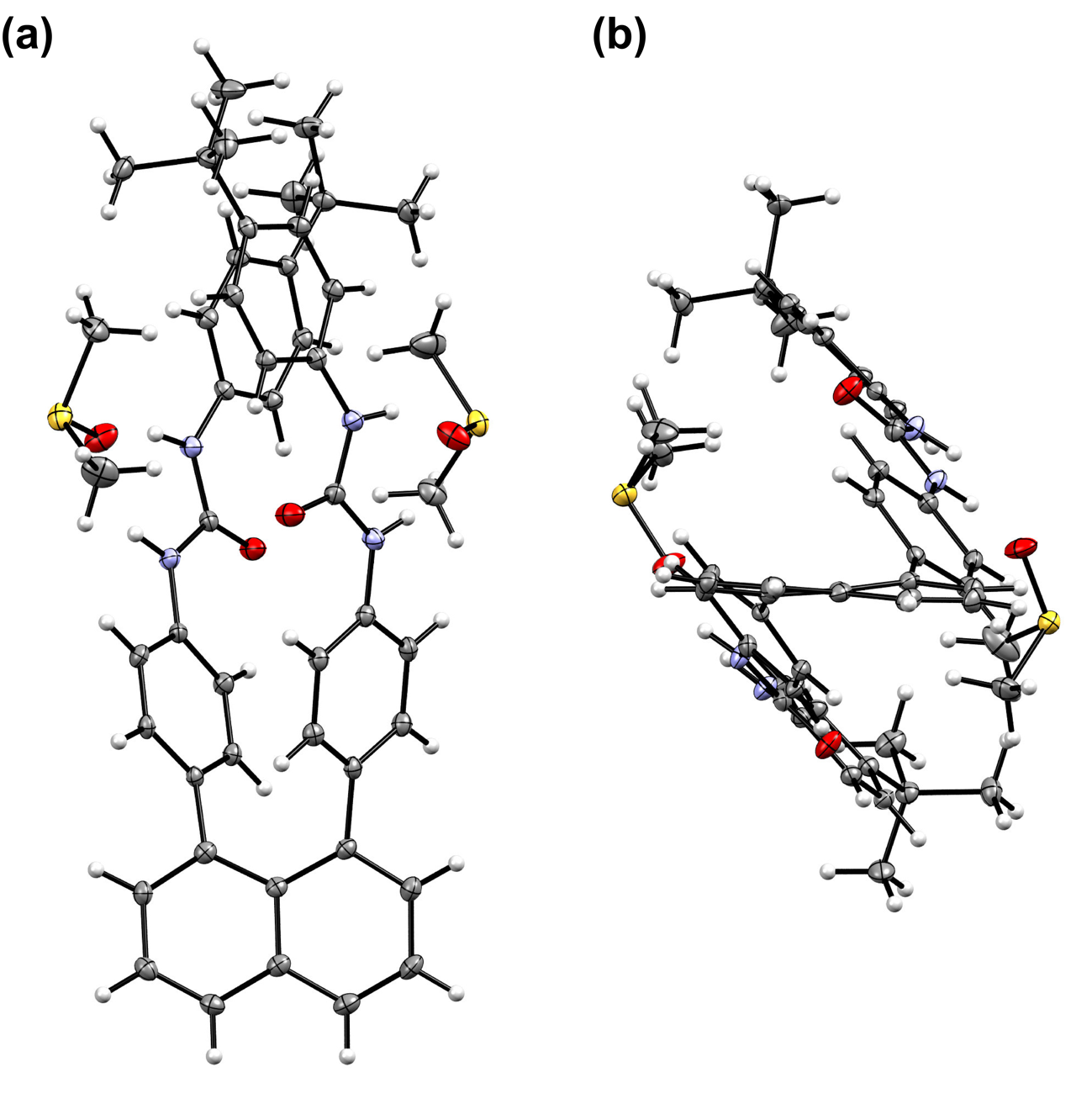
**Supplementary Figure 2.** 13C NMR spectrum of ***p-*2urea** in DMSO-*d*6.



**Supplementary Figure 3.** Heteronuclear single quantum correlation (HSQC) spectrum of ***p-*2urea** in DMSO-*d*6.



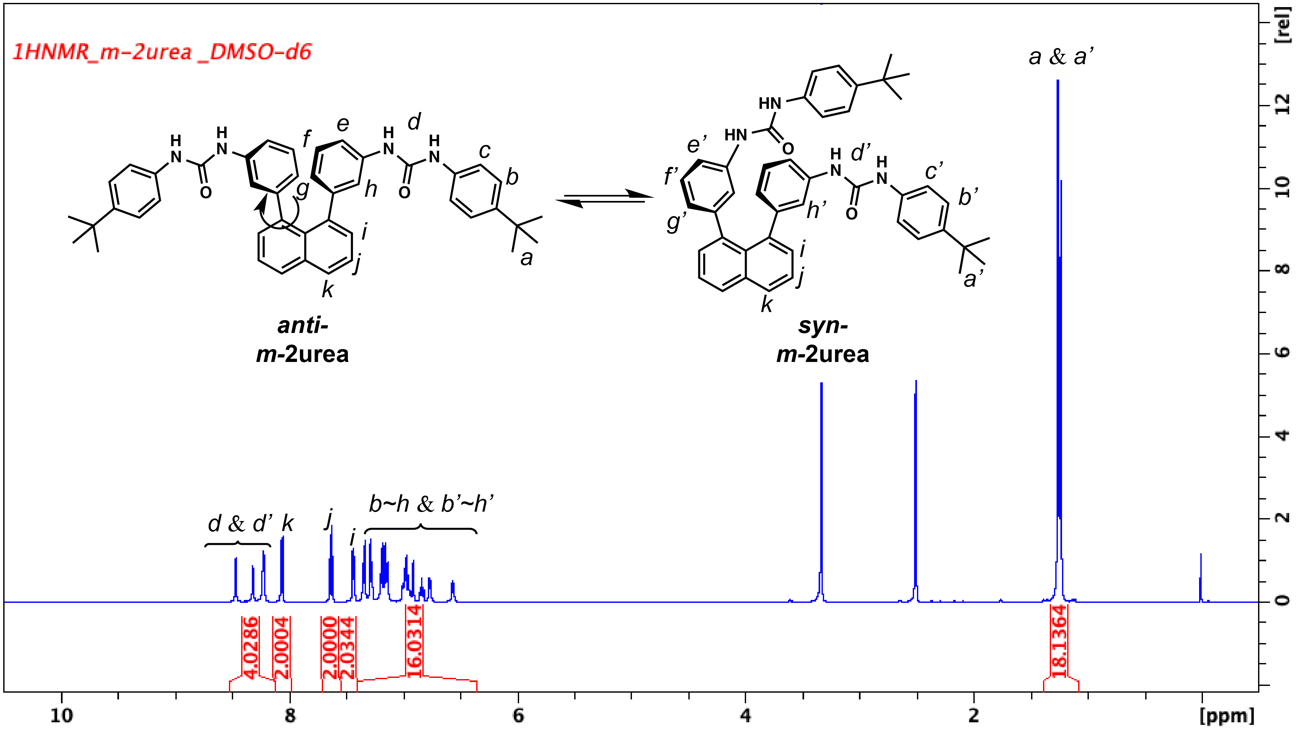
**Supplementary Figure 4.** Nuclear Overhauser effect spectroscopy (NOESY) results for ***p-*2urea** in DMSO-*d*6.



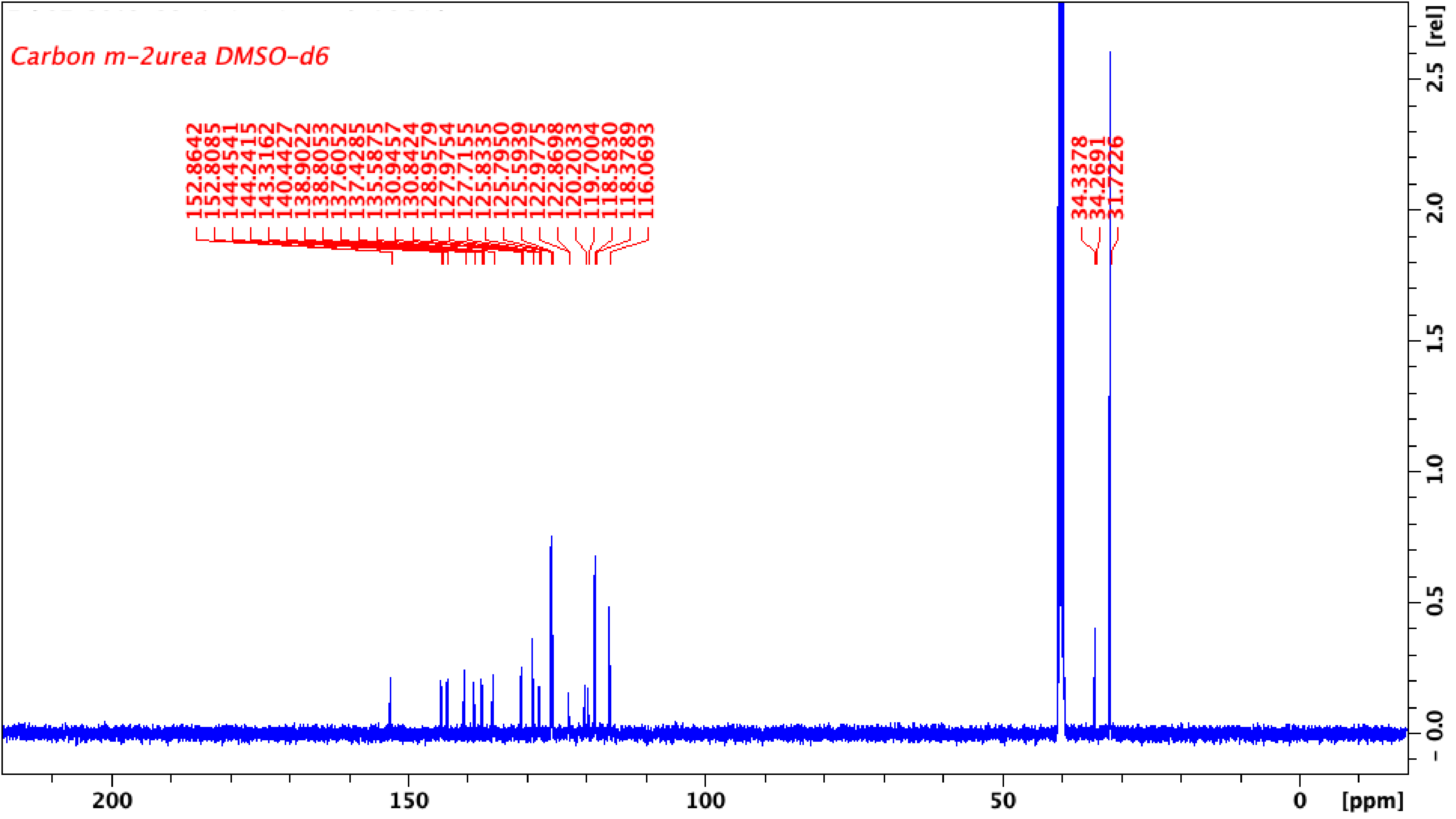
**Supplementary Figure 5.** (a) Top and (b) side views of the molecular structure of ***p-*2urea** hydrogen-bonded to the S=O groups of DMSO. Thermal ellipsoids are drawn at the 50% probability level.

**Supplementary Table 1.** Crystal data and structure refinement for ***p-*2urea**

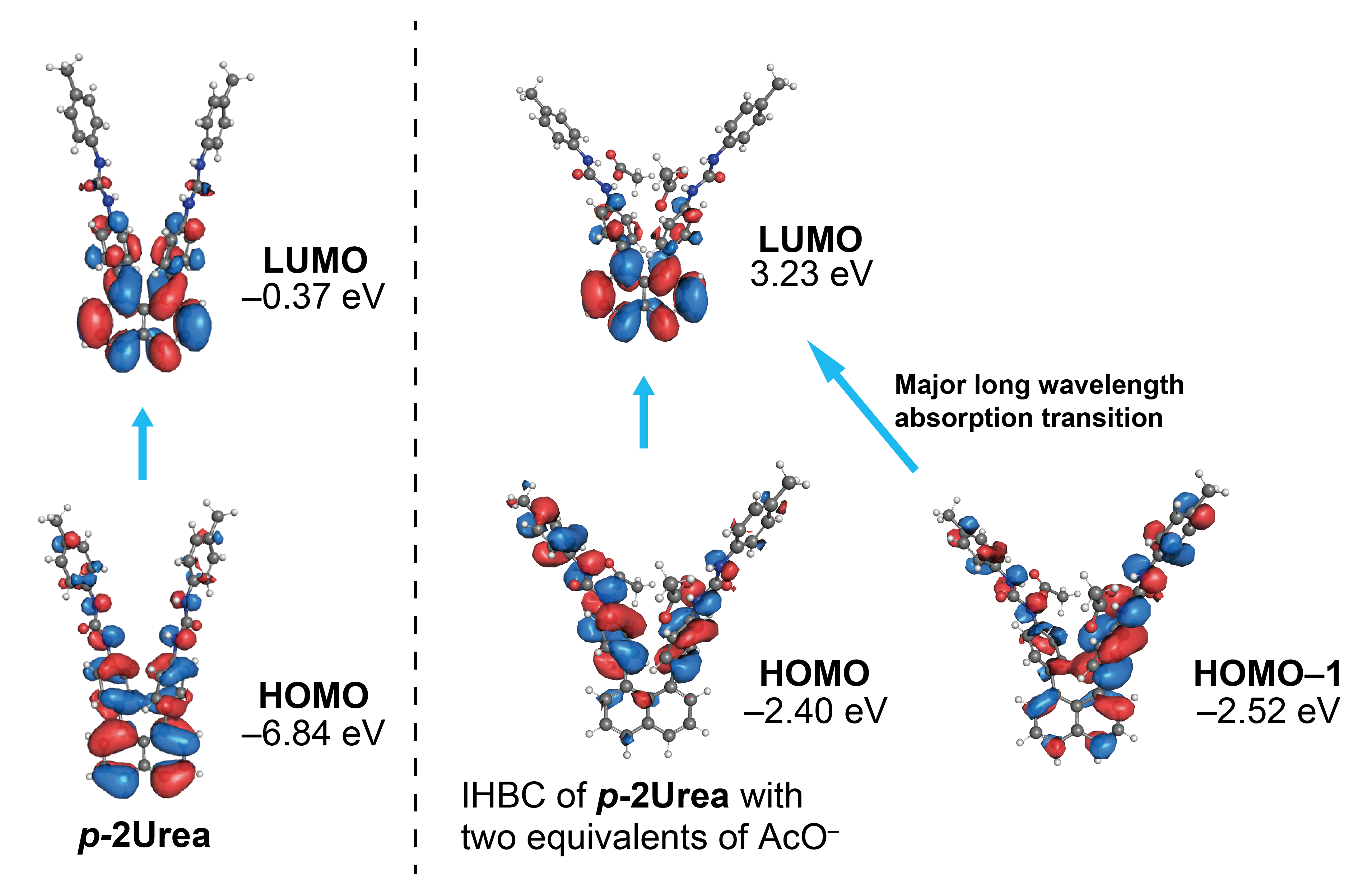
|  |  |
| --- | --- |
| Chemical formula Sum | C48H56N4O2 |
| Formula weight | 817.08 g/mol |
| Temperature | 90 K |
| Crystal system | Orthorhombic |
| Space group | Pna21 |
| *a* | 21.163(3) Å |
| *b* | 15.142(4) Å |
| *c* | 13.580(2) Å |
| *α* | 90° |
| *β* | 90° |
| *γ* | 90° |
| Volume | 4351.9(12) Å3 |
| Z | 4 |
| Reflection | 25690 |
| Unique reflection | 9232 |
| Goodness-of-fit on F2 | 1.042 |
| Final R indices [*I* > 2σ(*I*)], R1, wR2 | R1 = 0.0439, wR2 = 0.1260 |
| R indices (all data), R1, wR2 | R1 = 0.0468, wR2 = 0.1288 |



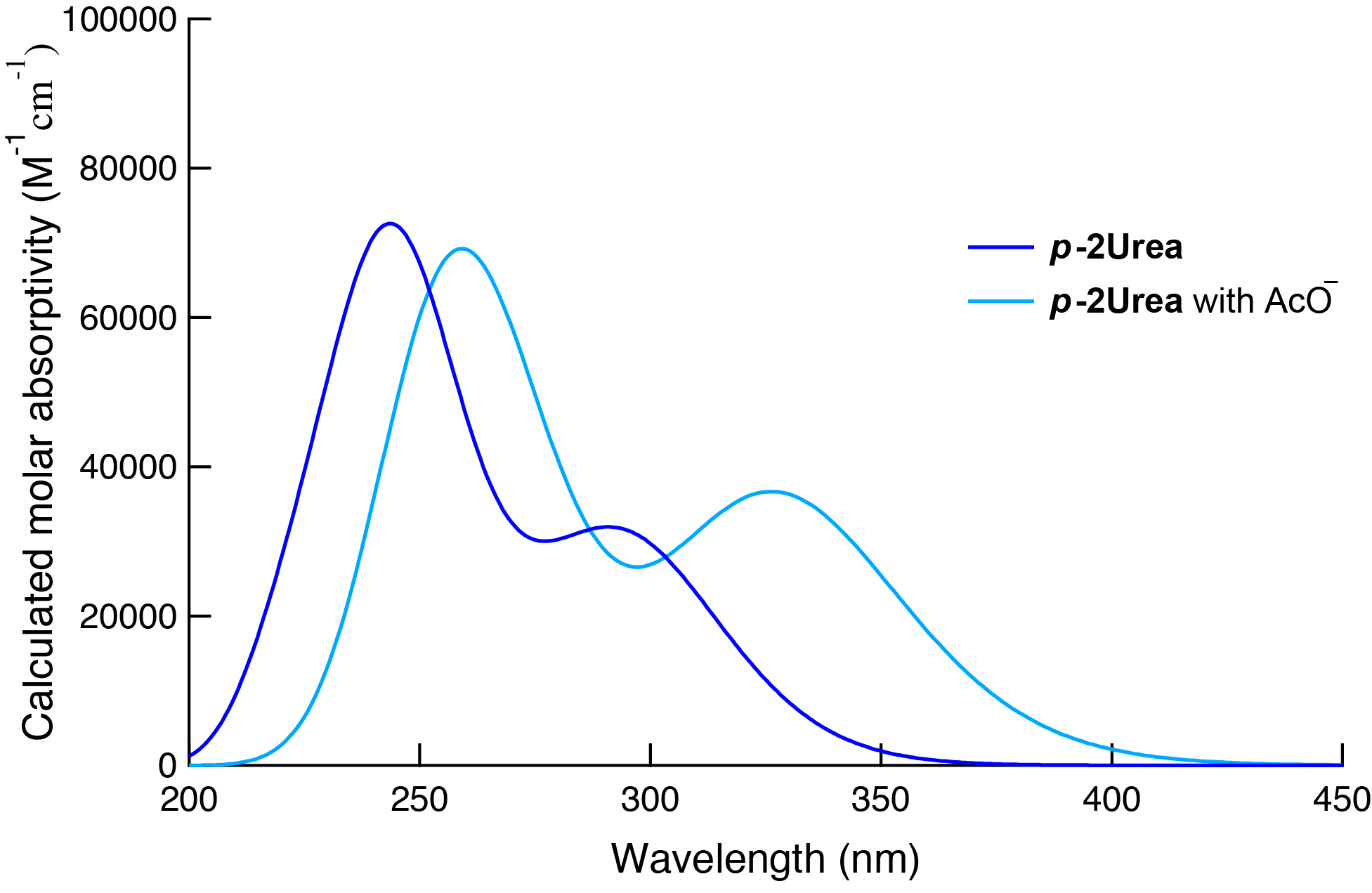
**Supplementary Figure 6.** ¹H NMR spectrum of ***m-*2urea** in DMSO-*d*6.



**Supplementary Figure 7.** 13C NMR spectrum of ***m-*2urea** in DMSO-*d*6.



**Supplementary Figure 8.** Frontier molecular orbital amplitude plots of the HOMO and LUMO of ***p*-2urea** (left) and the complex of ***p*-2urea** with two equivalents of AcO– (right). The geometry of ***p-*2urea** was first optimised at the B3LYP/6-31G (d, p) before TF-DFT excitation energy calculation were carried out at the CAM-B3LYP/6-31G+ (d) level of theory. The geometry of the complex of ***p*-2urea** with two equivalents of AcO– was first optimised at the CAM-B3LYP/6-31G+ (d) level of theory before TD-DFT excitation energy calculations were carried out at the CAM-B3LYP/6-31G+ (d) level.



**Supplementary Figure 9.** Calculated absorption spectrum of ***p-*2urea** and ***p-*2urea** with two equivalents of AcO–.

**Supplementary Table 2.** Calculated excitation energies and oscillator strengths from the ground state, with orbital configuration contributions, for the ground-state optimised geometry of ***p-*2urea**

|  |  |  |  |
| --- | --- | --- | --- |
| Excited state | Transition energy / eV | Oscillator strength *f* | Configuration and percentage contributiona |
| S1 | 4.193 (295 nm) | 0.6383 | HOMO→LUMO (85.1%) |
| S2 | 4.352 (285 nm) | 0.1230 | HOMO−1→LUMO (54.0%) |
| S3 | 4.434 (280 mm) | 0.0109 | HOMO−1→LUMO (20.4%) |
| S4 | 4.744 (261 nm) | 0.0340 | HOMO−1→LUMO (41.4%) |
| S5 | 4.805 (258 nm) | 0.001 | HOMO−1→LUMO+1 (58.4%) |

aPercentages for the single-particle contributions (*y*%) to the vertical excited states were calculated using the following expression:

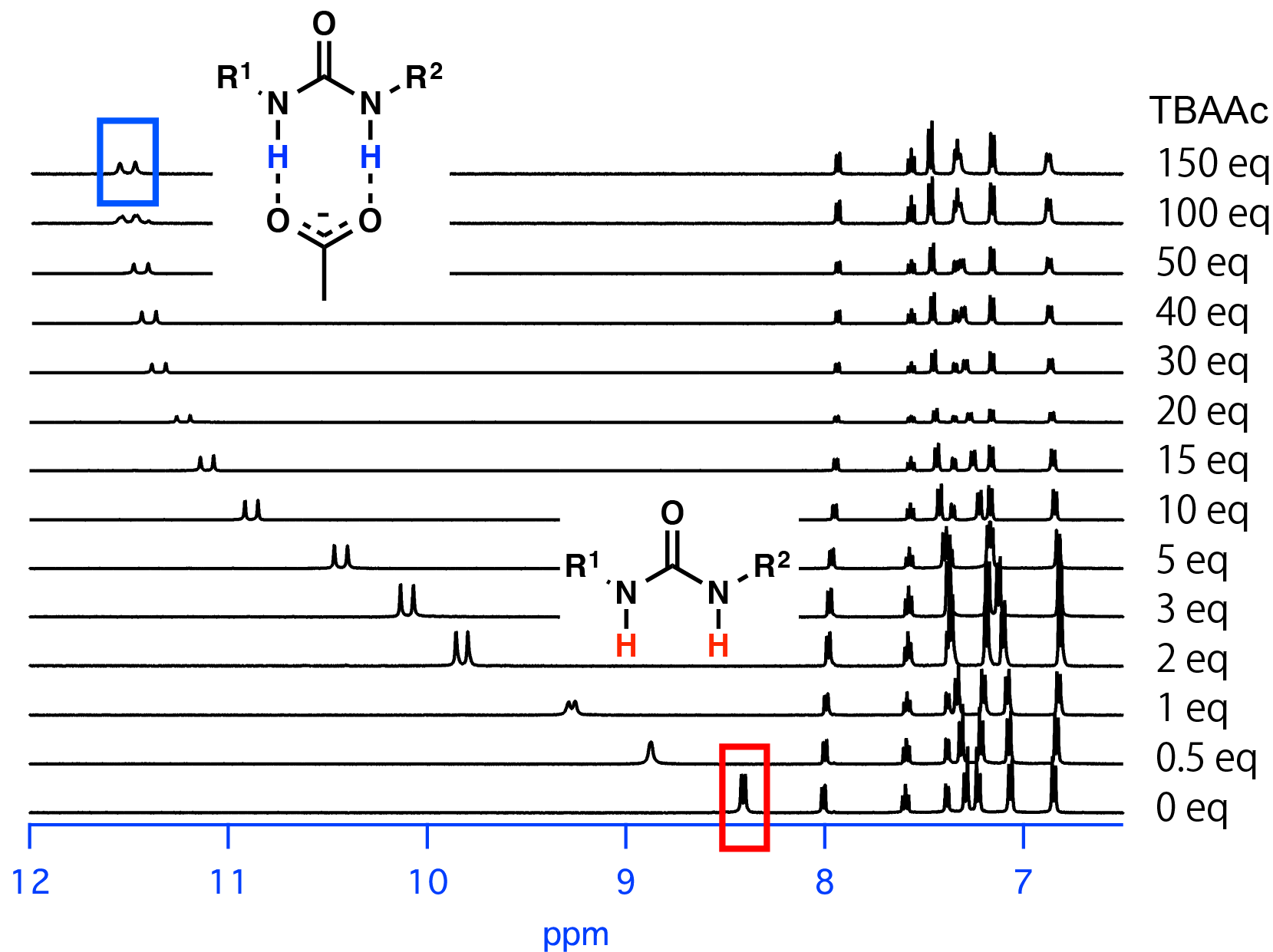
,

where ***xi*** is the single-particle transition corresponding to a given vertical excited state.

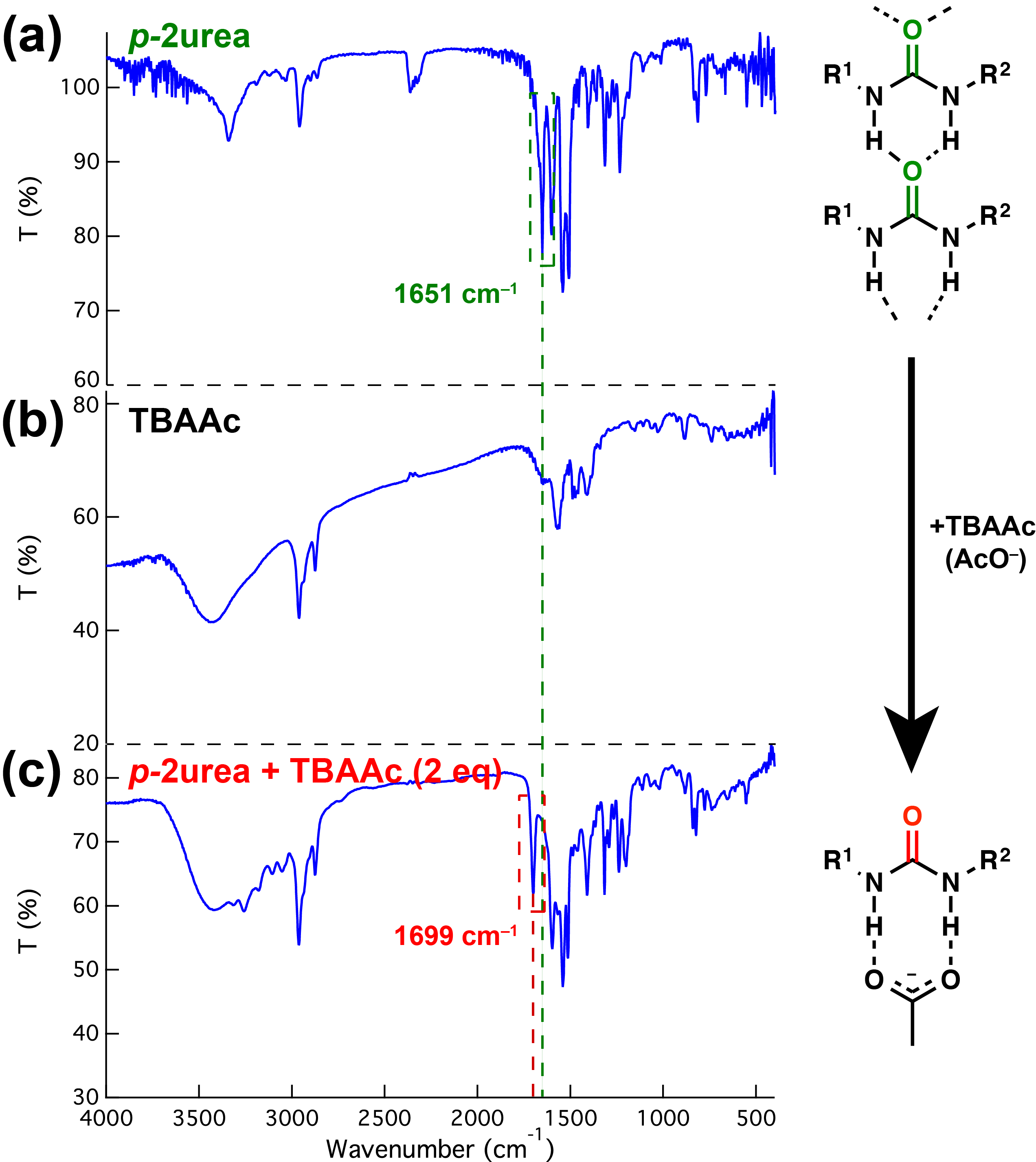
**Supplementary Table 3.** Calculated excitation energies and oscillator strengths from the ground-state, with orbital configuration contributions, for the ground-state optimised geometry of ***p-*2urea** with two equivalents of AcO–

|  |  |  |  |
| --- | --- | --- | --- |
| Excited state | Transition energy / eV | Oscillator strength *f* | Configuration and percentage contributiona |
| S1 | 3.704 (335 nm) | 0.2356 | HOMO→LUMO (69.6%) |
| S2 | 3.805 (326 nm) | 0.6503 | HOMO−1→LUMO (64.8%) |
| S3 | 4.237 (293 nm) | 0.0776 | HOMO−1→LUMO+3 (33.7%) |
| S4 | 4.613 (269 nm) | 0.3360 | HOMO→LUMO+3 (54.6%) |
| S5 | 4.660 (266 nm) | 0.1118 | HOMO→LUMO+8 (10.5%) |

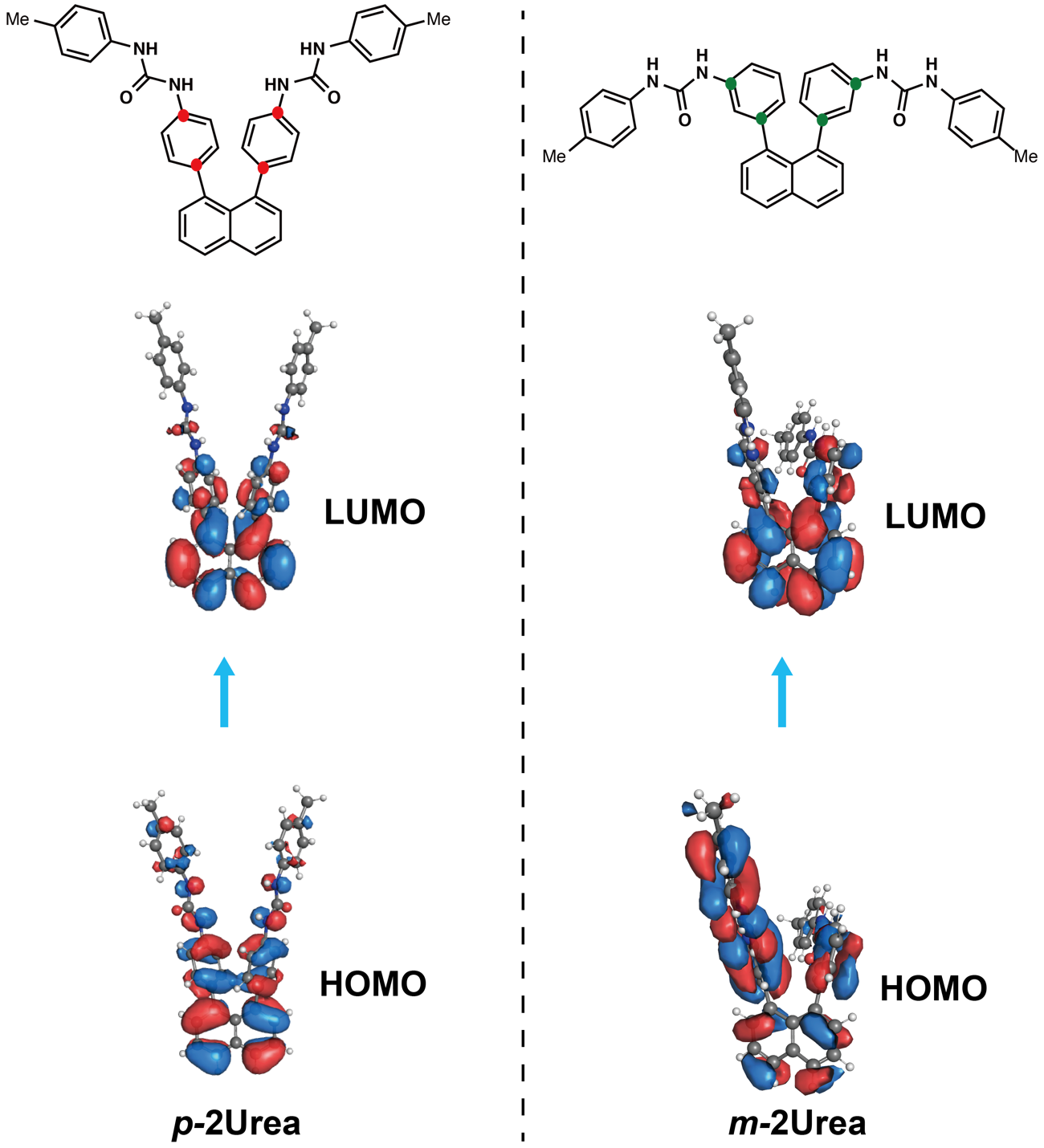
aThe percentages were calculated using the expression given in the footnote of Supplementary Table 2.



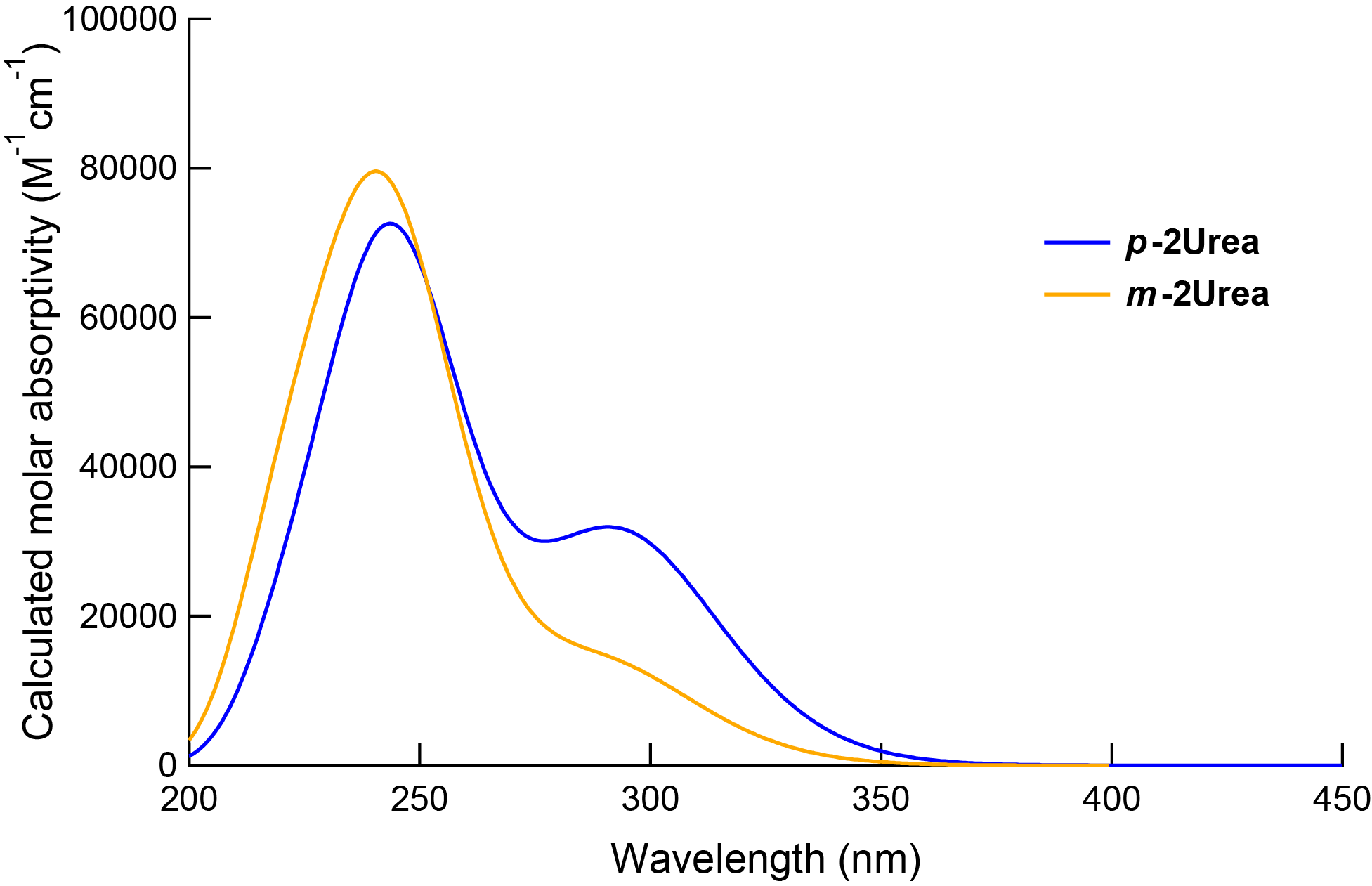
**Supplementary Figure 10.** ¹H NMR spectra acquired over the course of titrating a solution of ***p*-2urea** (2.0 mM) with tetrabutylammonium acetate (TBAAc) in DMSO-*d*₆.



**Supplementary Figure 11.** FT-IR spectra of ***p*-2urea** and ***p*-2urea**–acetate-ion complex in solid-state. (a) FT-IR spectra of TBAAc. (b) FT-IR spectra of ***p*-2urea**. (c) FT-IR spectra of the mixture of ***p*-2urea** and TBAAc.



**Supplementary Figure 12.** Frontier molecular orbital amplitude plots of the HOMOs and LUMOs of ***p*-2urea** (left) and ***m-*2urea** (right). The geometry was first optimised at the B3LYP/6-31G (d, p) level of theory before TD-DFT excitation energy calculations were carried out at the CAM-B3LYP/6-31G+ (d) level.

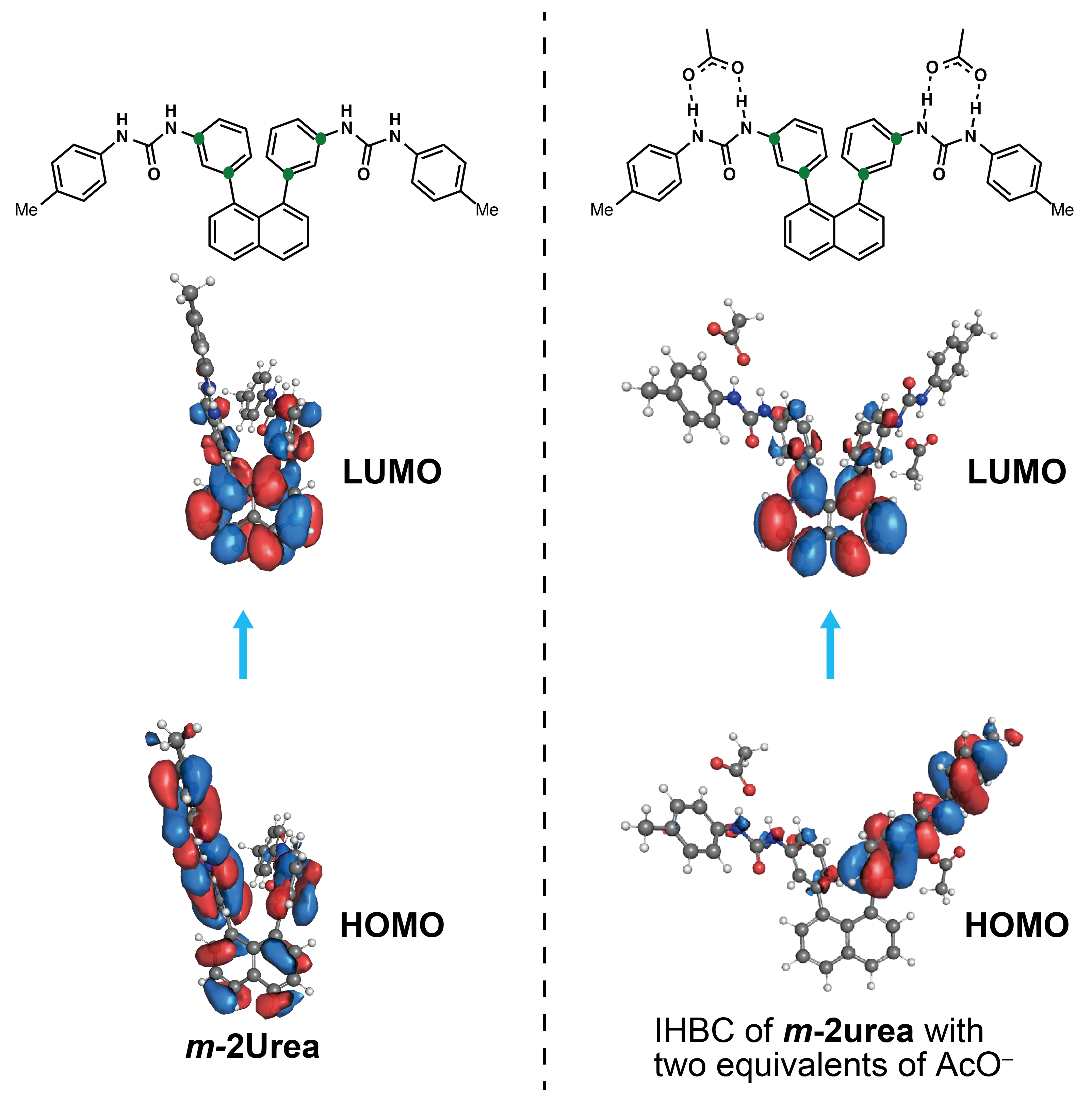


**Supplementary Figure 13.** Calculated absorption spectra of ***p-*2urea** and ***m-*2urea**.

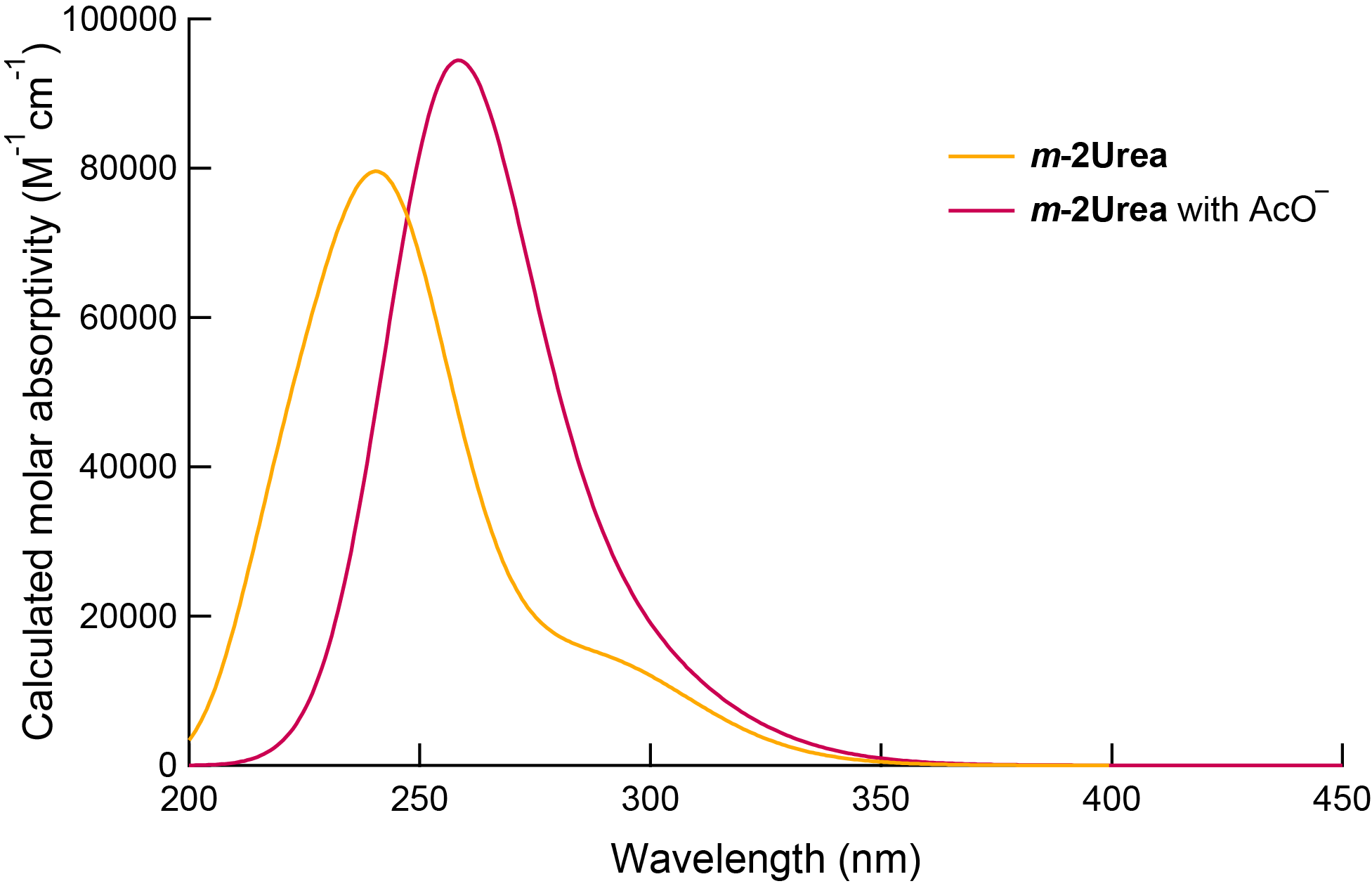
**Supplementary Table 4.** Calculated excitation energies and oscillator strengths from the ground state, with orbital configuration contributions, for the ground-state optimised geometry of ***m-*2urea**

|  |  |  |  |
| --- | --- | --- | --- |
| Excited state | Transition energy / eV | Oscillator strength *f* | Configuration and percentage contributiona |
| S1 | 4.267 (291 nm) | 0.3153 | HOMO→LUMO (51.3%) |
| S2 | 4.427 (280 nm) | 0.0056 | HOMO−6→LUMO (31.6%) |
| S3 | 4.662 (266 nm) | 0.0061 | HOMO→LUMO (22.1%) |
| S4 | 4.779 (259 nm) | 0.0338 | HOMO→LUMO+4 (26.2%) |
| S5 | 4.819 (257 nm) | 0.0092 | HOMO−1→LUMO+2 (20.4%) |

aThe percentages were calculated using the expression given in the footnote of Supplementary Table 2.



**Supplementary Figure 14.** Frontier molecular orbital amplitude plots of the HOMO and LUMO of ***m*-2urea** (left) and the complex of ***m*-2urea** with two equivalents of AcO– (right). The geometry of ***m-*2urea** was first optimised at the B3LYP/6-31G (d, p) level of theory before TD-DFT excitation energy calculations were carried out at the CAM-B3LYP/6-31G+ (d) level. The geometry of the complex of ***m*-2urea** with two equivalents of AcO– was first optimised at the CAM-B3LYP/6-31G+ (d) level of theory before TD-DFT excitation energy calculations were carried out at the CAM-B3LYP/6-31G+ (d) level.

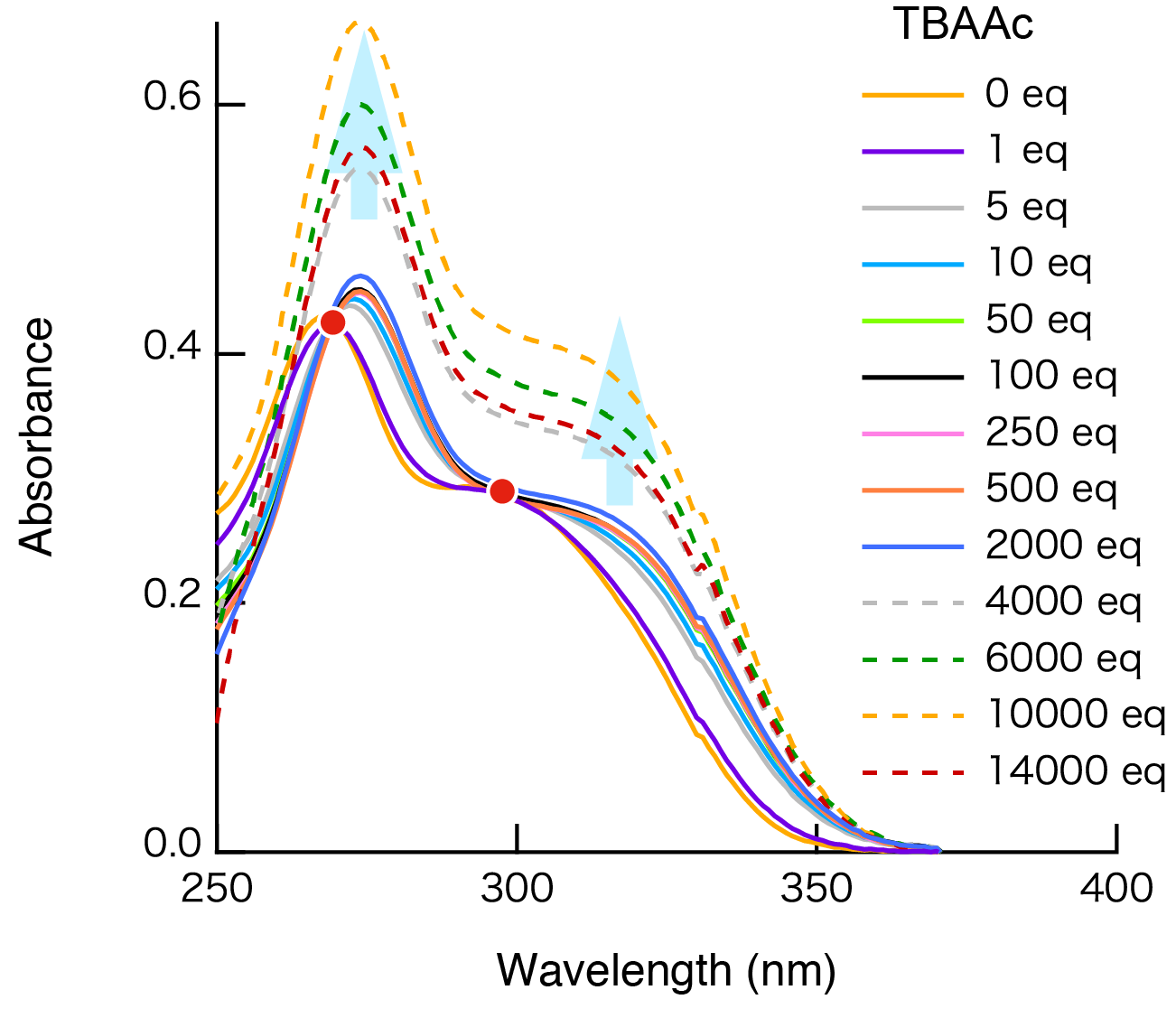


**Supplementary Figure 15.** Calculated absorption spectra of ***m-*2urea** and ***m-*2urea** with two equivalents of AcO–.

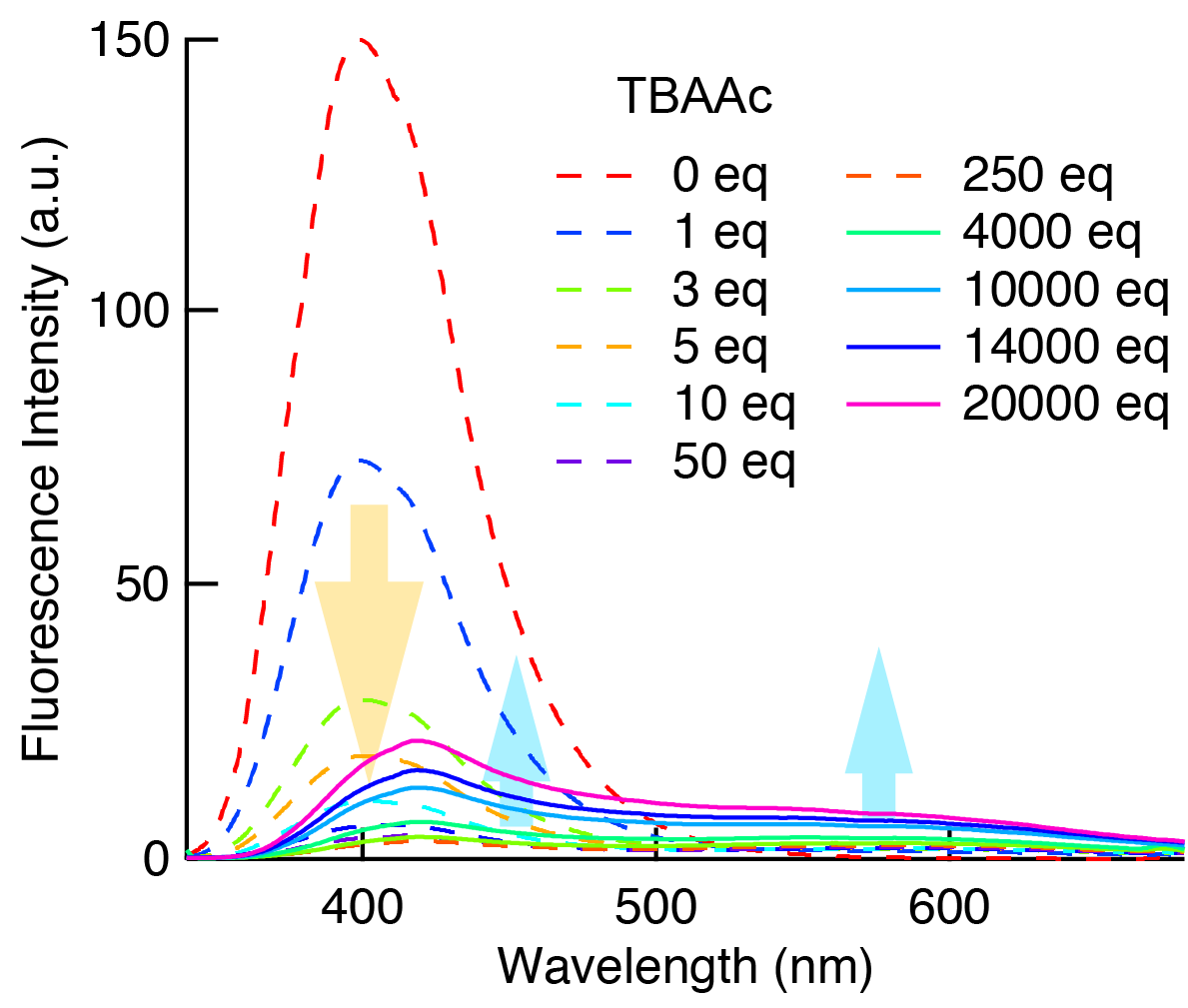
**Supplementary Table 5.** Calculated excitation energies and oscillator strengths from the ground state, with orbital configuration contributions, for the ground-state optimised geometry of the complex ***m-*2urea** and two equivalents of AcO–

|  |  |  |  |
| --- | --- | --- | --- |
| Excited state | Transition energy / eV | Oscillator strength *f* | Configuration and percentage contribution**a** |
| S1 | 4.054 (306 nm) | 0.0173 | HOMO→LUMO (49.2%) |
| S2 | 4.120 (301 nm) | 0.1214 | HOMO−1→LUMO (43.6%) |
| S3 | 4.328 (286 nm) | 0.2277 | HOMO−6→LUMO (71.0%) |
| S4 | 4.458 (278 nm) | 0.0300 | HOMO−6→LUMO+4 (31.3%) |
| S5 | 4.761 (260 nm) | 0.1138 | HOMO−11→LUMO (30.9%) |

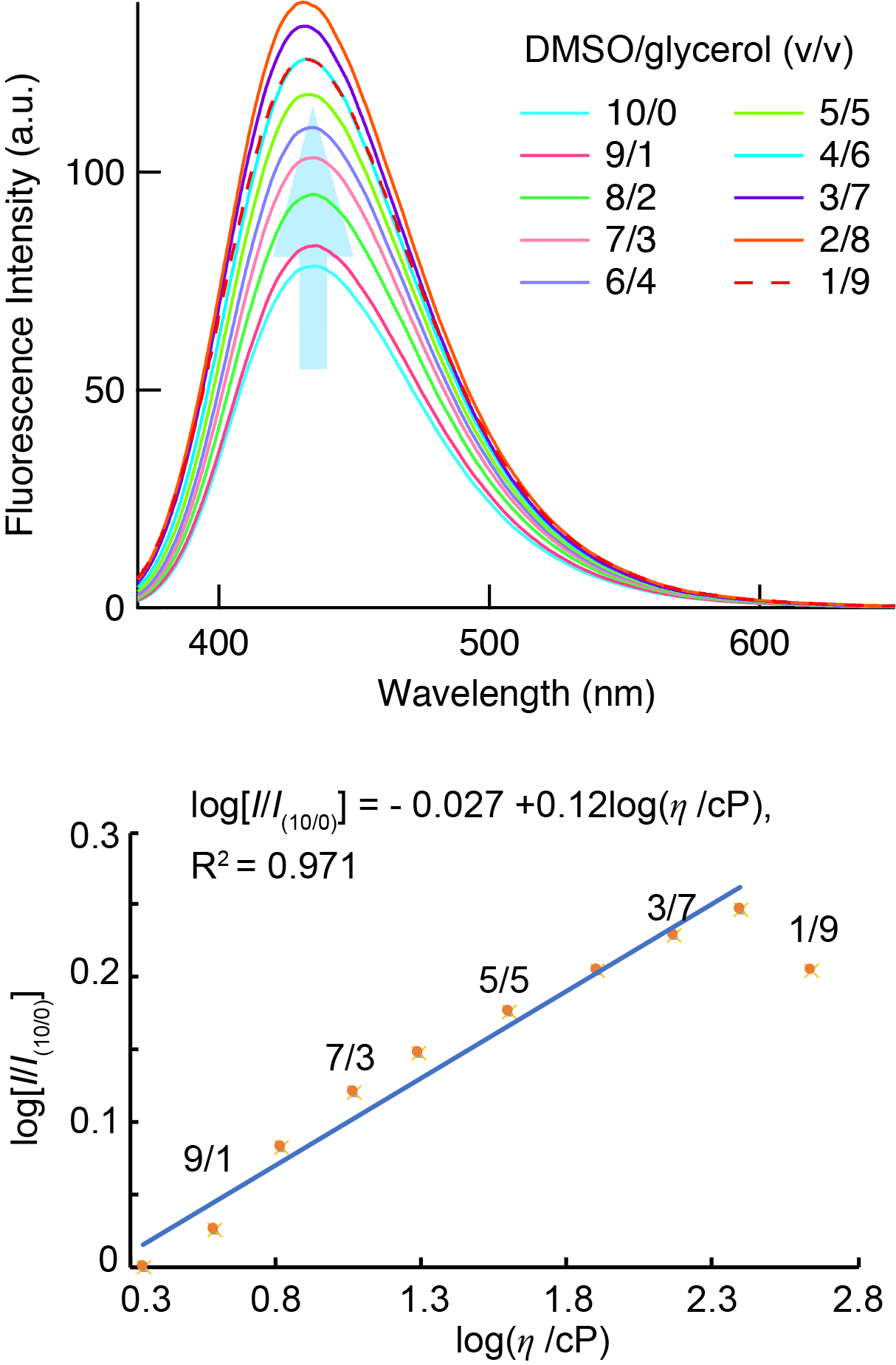
aThe percentages were calculated using the expression given in the footnote of Supplementary Table 2.



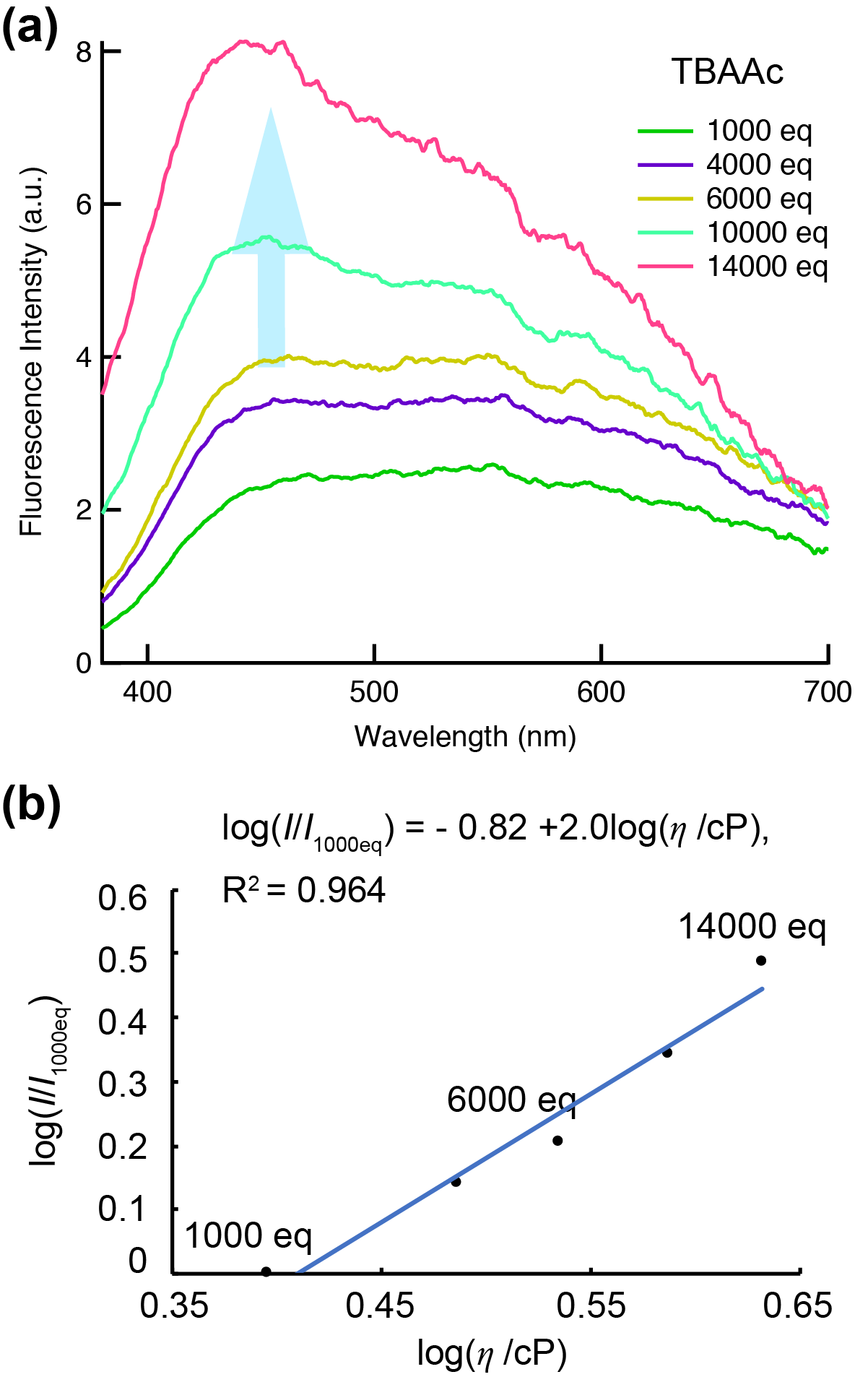
**Supplementary Figure 16.** Absorbance spectra of ***p-*1urea** in the absence and presence of TBAAc.



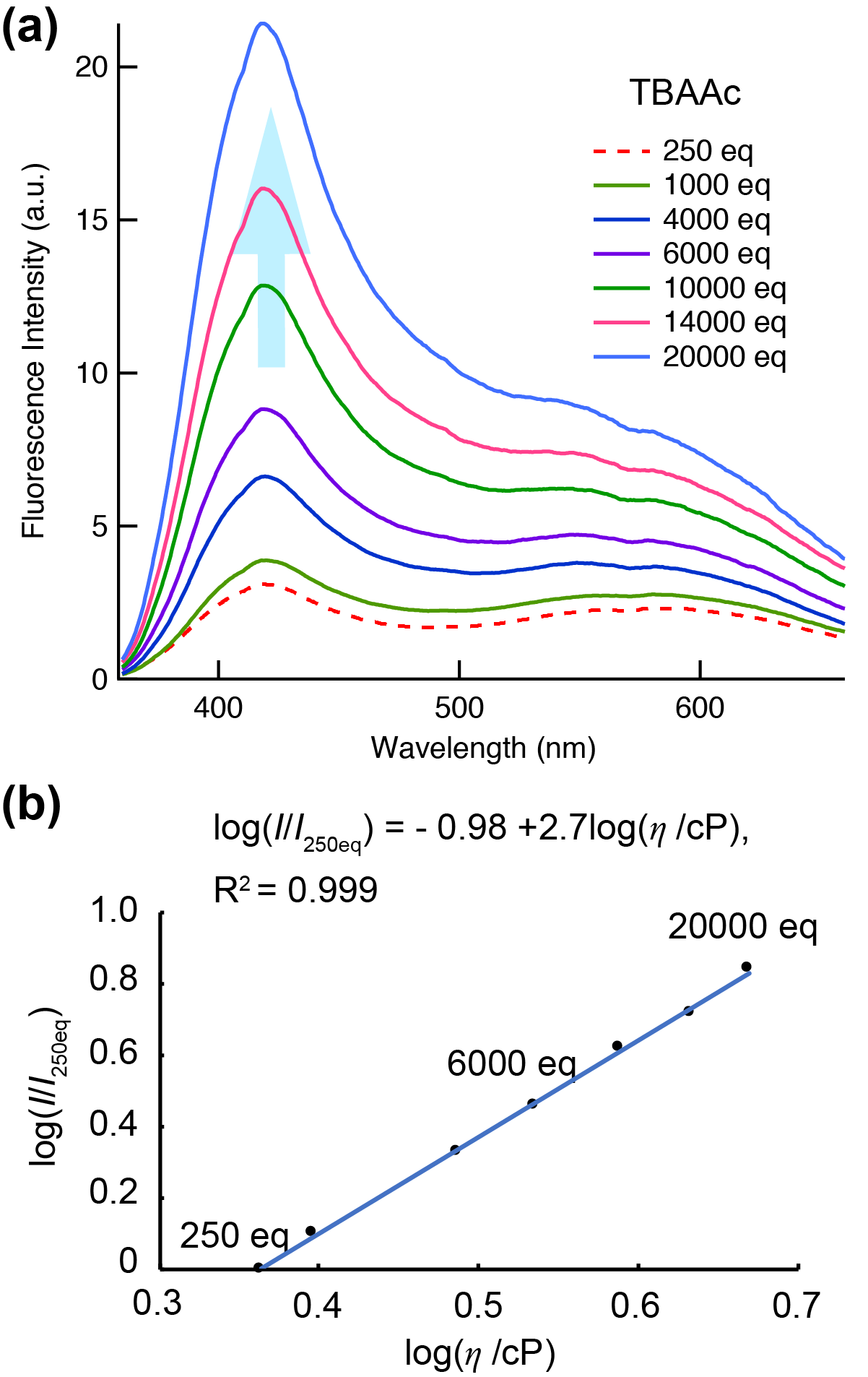
**Supplementary Figure 17.** Fluorescence spectra of a DMSO solution of ***p-*1urea** (150 µM, *λ*ex = 336 nm) in the absence and presence of various equivalents of TBAAc.



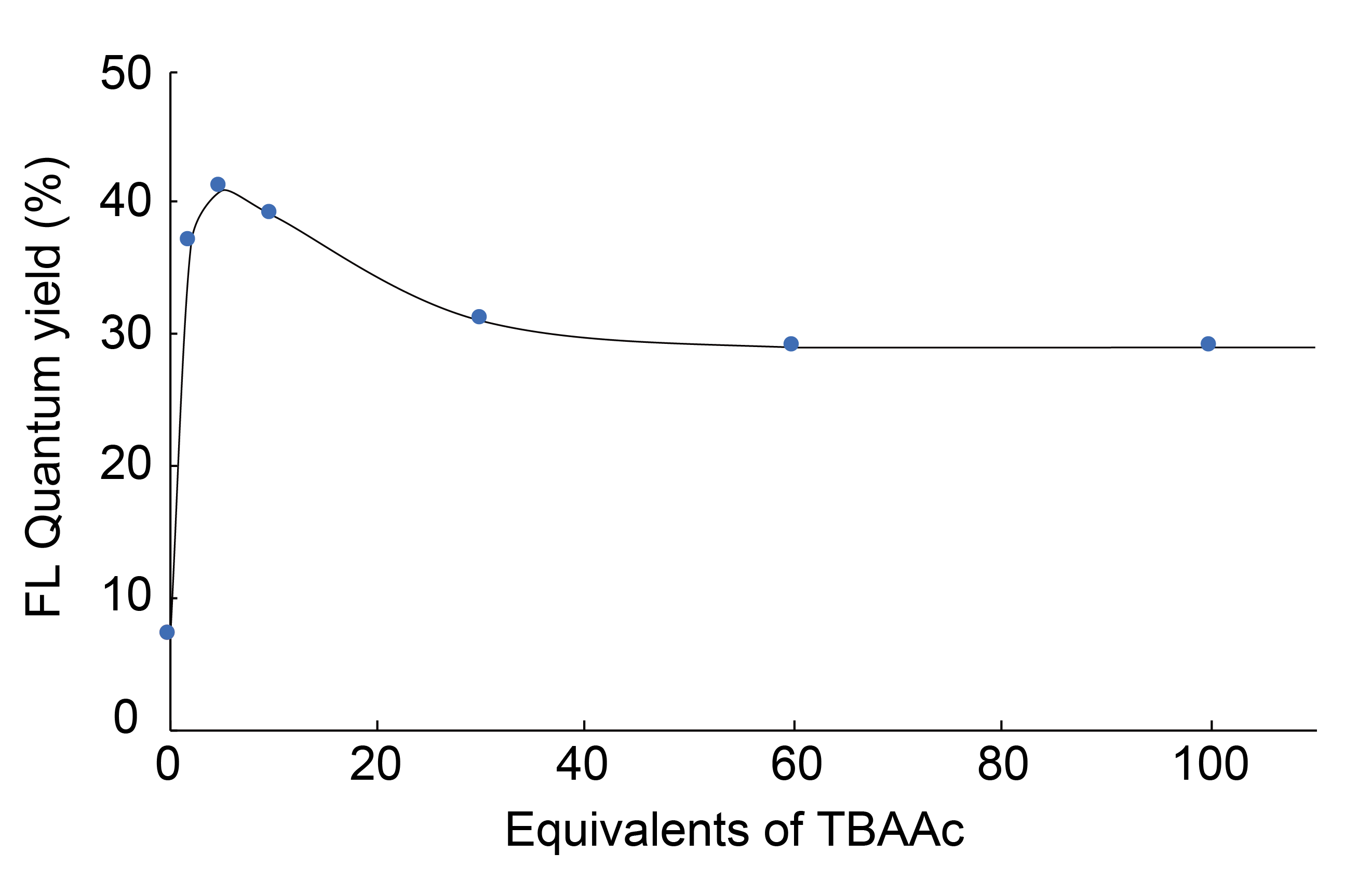
**Supplementary Figure 18.** Viscosity-sensitivity of the ***p*-2urea** complex and fluorescence intensity. (a) Fluorescence spectra of ***p*-2urea** in mixed solvents with different fractions of glycerol [DMSO/glycerol (v/v) = 10/0, 9/1, 8/2, 7/3, 6/4, 5/5, 4/6, 3/7, 2/8, and 1/9]. (b) Linear relationship between log(*I/I*(v/v)) and log(η /cP) in mixtures of DMSO and glycerol ([***p*-2urea**] = 1.5 µM, *λ*ex = 359 nm).



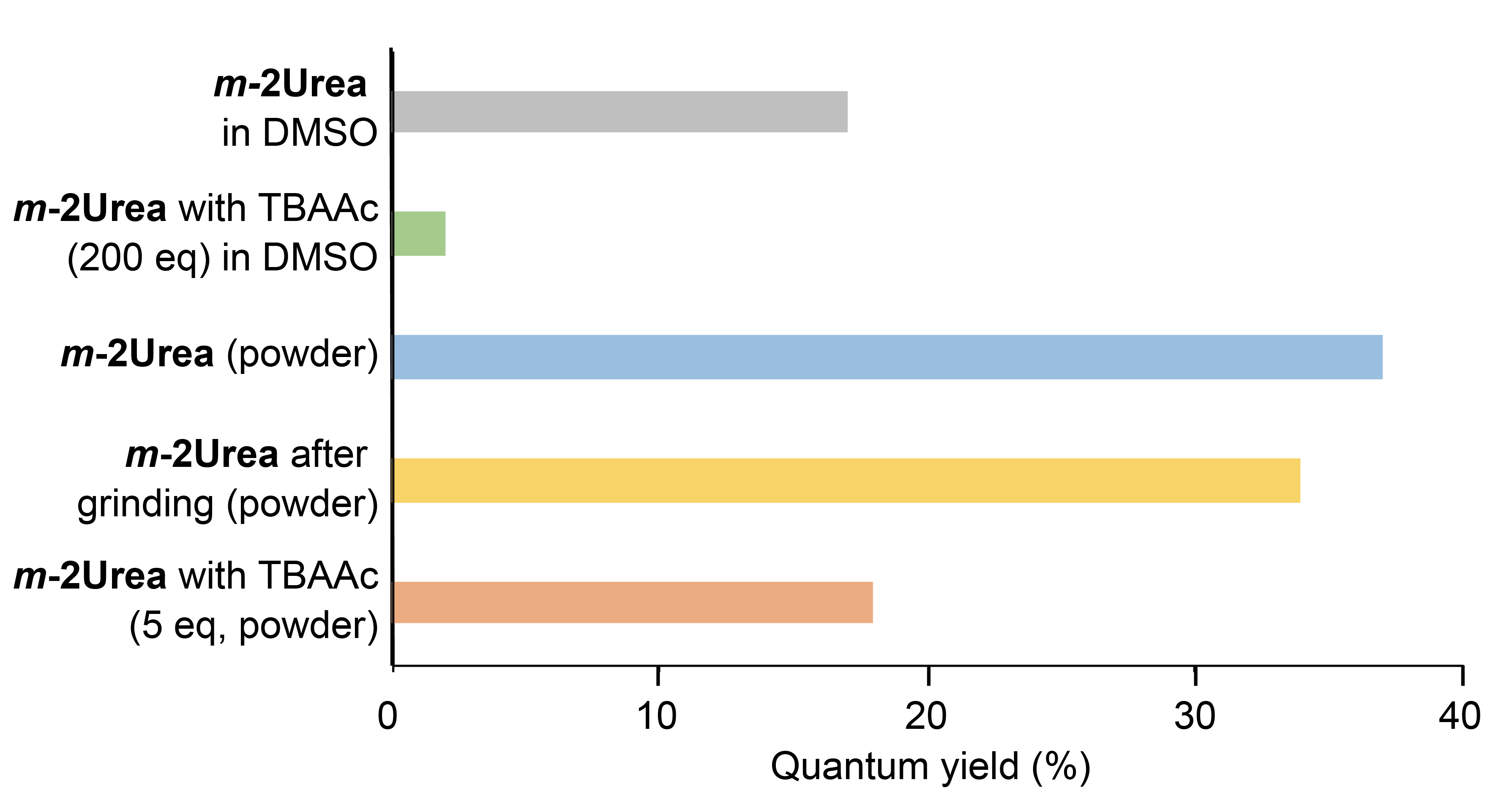
**Supplementary Figure 19.** (a) Fluorescence spectra of ***m*-2urea** (150 µM, *λ*ex= 332 nm) with the addition of various excess amounts of TBAAc in DMSO. (b) Log–log plot of the ratio of fluorescence intensities at 470.5 nm as a function of solvent viscosity.



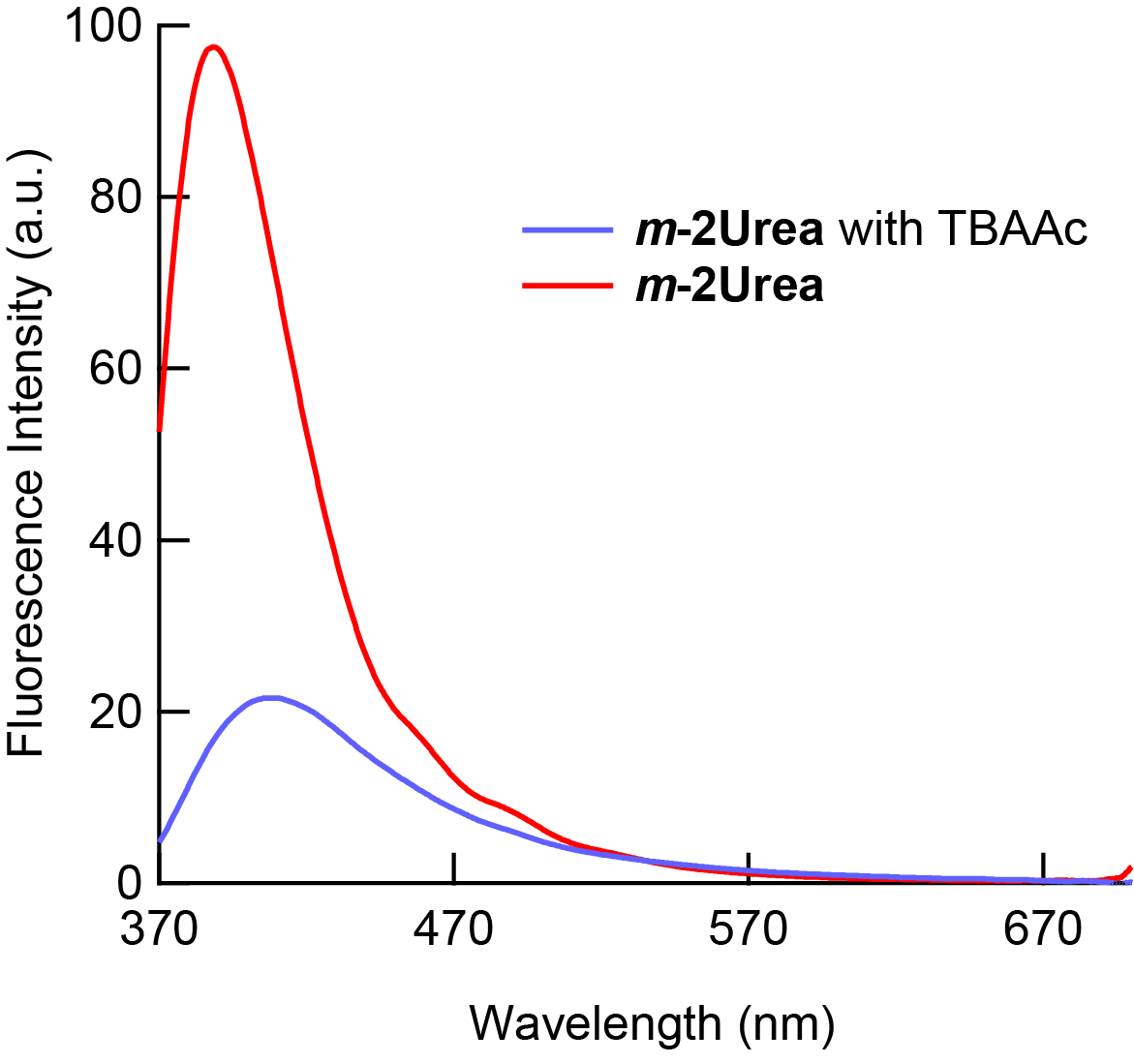
**Supplementary Figure 20.** (a) Fluorescence spectra of ***p*-1urea** (150 µM, *λ*ex= 336 nm) with the addition of various excess amounts of TBAAc in DMSO. (b) Log–log plot of the ratio of fluorescence intensities at 418 nm as a function of solvent viscosity.



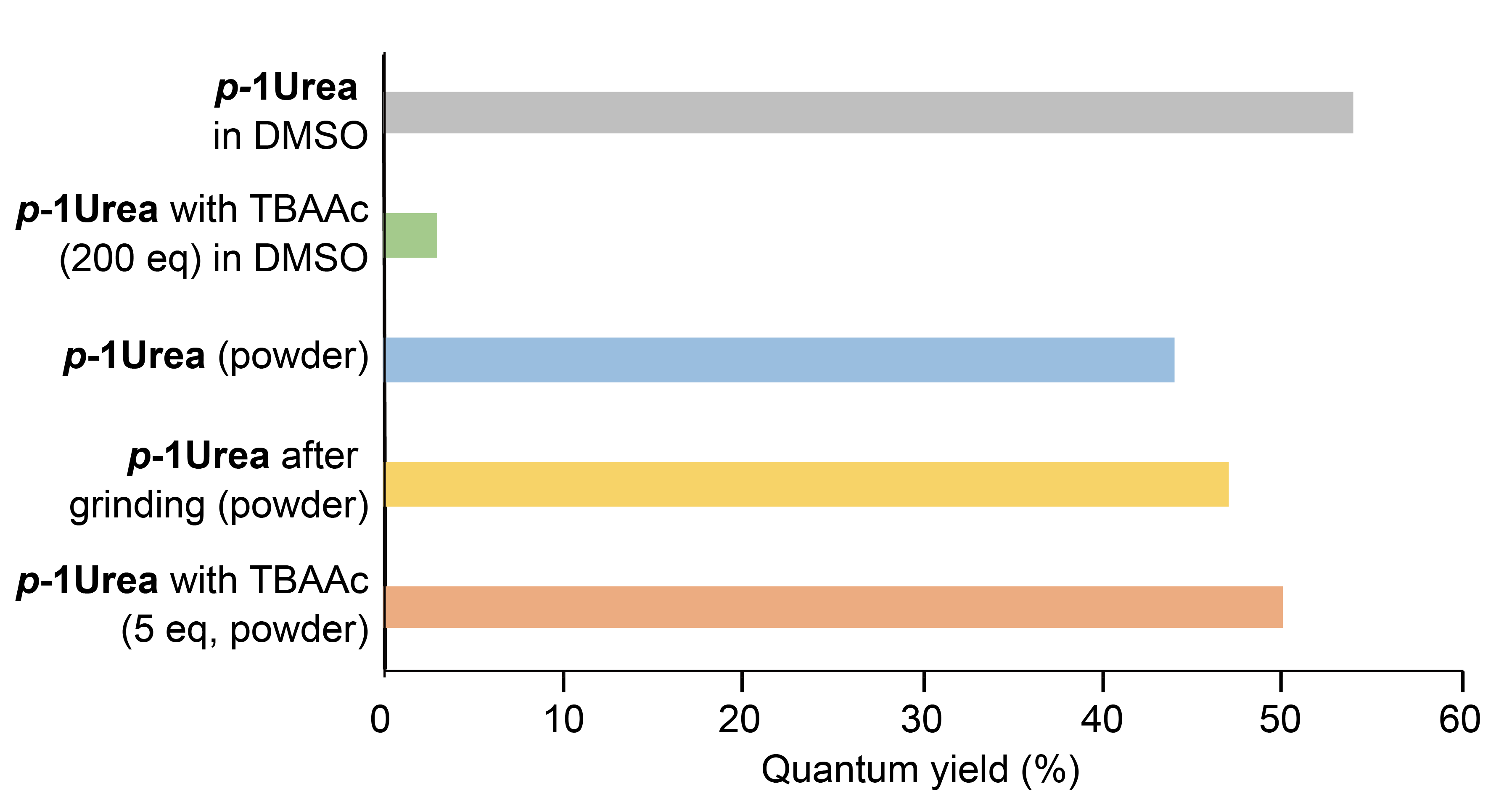
**Supplementary Figure 21.** Fluorescence quantum yields of ***p-*2urea** powders in the presence of various amounts of TBAAc and in its absence.



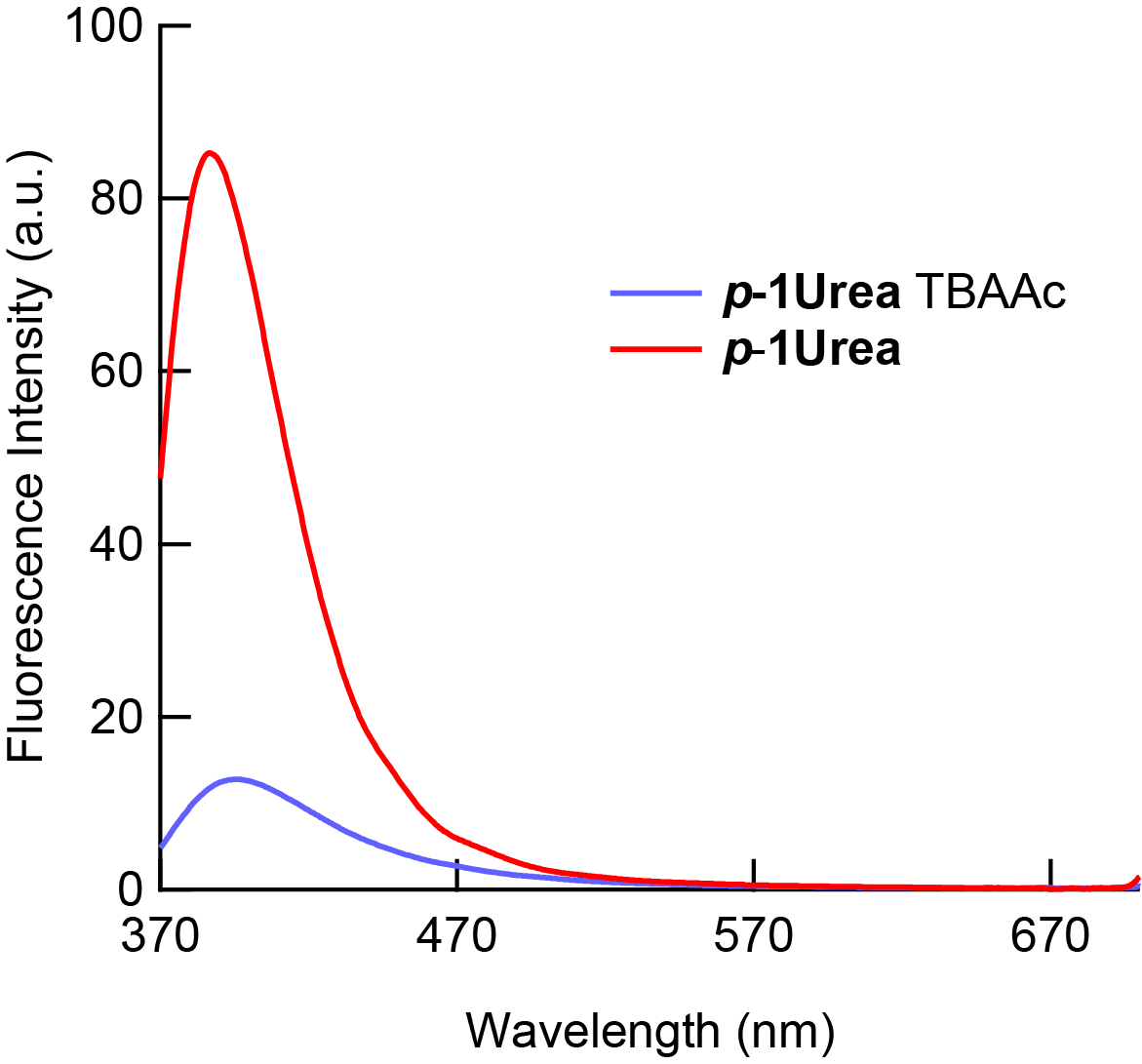
**Supplementary Figure 22.** Absolute fluorescence quantum yields of ***m*-2urea** powder and ***m*-2urea–**DMSO solution in the absence and presence of TBAAc.



**Supplementary Figure 23.** Solid-state fluorescence spectra of ***m*-2urea** in the presence and absence of 5 equiv of TBAAc when excited at 323 nm.



**Supplementary Figure 24.** Absolute fluorescence quantum yields of ***p*-1urea** powder and ***p*-1urea**–DMSO solution in the absence and presence of TBAAc.



**Supplementary Figure 25.** Solid-state fluorescence spectra of ***p*-1urea** in the presence and absence of 5 equiv of TBAAc when excited at 323 nm.

Table S6. Structure of ***p-*2urea**, S0 [DFT/B3LYP/6-31G (d, p), *E*sp = -1836.90938116 hartree].

|  |  |  |  |
| --- | --- | --- | --- |
| atom | x[Å] | y[Å] | z[Å] |
| C | -7.70735 | -4.82948 | 0.69874 |
| H | -7.03939 | -3.4336 | -1.56866 |
| C | -6.35664 | -4.29338 | 0.28748 |
| C | -6.18357 | -3.60848 | -0.92147 |
| C | -5.22278 | -4.48247 | 1.08574 |
| H | -5.32238 | -5.0058 | 2.03377 |
| C | -4.93405 | -3.14058 | -1.31401 |
| H | -4.83326 | -2.60649 | -2.25683 |
| C | -3.9602 | -4.02387 | 0.71248 |
| C | -3.80607 | -3.34317 | -0.50407 |
| H | -3.10088 | -4.18111 | 1.34766 |
| H | -2.62942 | -2.40704 | -1.88753 |
| N | -2.57544 | -2.84056 | -0.9776 |
| C | -1.34027 | -2.86159 | -0.34656 |
| O | -1.14645 | -3.34512 | 0.76153 |
| H | -0.62448 | -1.85281 | -1.99405 |
| N | -0.3479 | -2.27559 | -1.12004 |
| H | 1.04188 | -3.18386 | 1.05419 |
| C | 1.00514 | -2.06549 | -0.7839 |
| C | 1.61847 | -2.58459 | 0.365 |
| H | -2.65939 | 2.32257 | 1.84522 |
| H | -4.86987 | 2.4879 | 2.19089 |
| H | -0.6449 | 1.8116 | 1.9728 |
| C | 1.77216 | -1.29561 | -1.67341 |
| H | 1.31397 | -0.8987 | -2.57688 |
| C | 2.96074 | -2.30225 | 0.61013 |
| H | 1.30062 | 0.88135 | 2.56699 |
| C | -4.96022 | 3.07185 | 1.27703 |
| H | 3.41791 | -2.69679 | 1.51328 |
| H | -7.07122 | 3.33763 | 1.51477 |
| C | 1.75917 | 1.28238 | 1.66555 |
| N | -0.36598 | 2.2462 | 1.10538 |
| N | -2.59442 | 2.80707 | 0.96211 |
| C | -6.207 | 3.55275 | 0.8913 |
| H | 3.66757 | 0.42628 | 2.11427 |
| C | 3.09739 | 1.02018 | 1.40758 |
| C | 3.10804 | -1.025 | -1.41171 |
| C | 0.99024 | 2.04917 | 0.7749 |
| C | -3.82173 | 3.3251 | 0.4967 |
| C | 3.73039 | -1.50698 | -0.25069 |
| C | -1.35326 | 2.85629 | 0.34435 |
| C | 3.72057 | 1.50782 | 0.24935 |
| C | 1.6041 | 2.5739 | -0.37121 |
| C | -6.36666 | 4.30126 | -0.28114 |
| H | 3.67687 | -0.42865 | -2.11744 |
| O | -1.15104 | 3.38097 | -0.74332 |
| C | -3.9623 | 4.07015 | -0.68329 |
| C | 2.94886 | 2.30002 | -0.61245 |
| C | 5.18239 | -1.28301 | 0.0071 |
| C | 5.17459 | 1.29282 | -0.00429 |
| C | -7.71465 | 4.85061 | -0.68376 |
| H | 1.02635 | 3.17218 | -1.06027 |
| C | -5.22225 | 4.54052 | -1.0505 |
| H | 5.4405 | -3.39047 | 0.16047 |
| C | 5.8367 | 0.00689 | 0.00232 |
| H | 5.42056 | 3.40179 | -0.15679 |
| C | 5.93347 | 2.445 | -0.16358 |
| C | 5.94767 | -2.43063 | 0.16856 |
| H | -3.0949 | 4.26601 | -1.29639 |
| H | 3.40646 | 2.69888 | -1.5135 |
| C | 7.33831 | 2.42297 | -0.25897 |
| C | 7.28135 | 0.01122 | 0.00434 |
| C | 7.35209 | -2.40018 | 0.26785 |
| H | -5.31129 | 5.11384 | -1.97025 |
| C | 7.99965 | 1.22724 | -0.13964 |
| H | 7.88659 | 3.35283 | -0.37712 |
| C | 8.00653 | -1.20048 | 0.15034 |
| H | 7.90562 | -3.32671 | 0.3876 |
| H | 9.08552 | 1.18742 | -0.15155 |
| H | 9.0921 | -1.15412 | 0.16533 |
| H | -8.52055 | -4.2084 | 0.31045 |
| H | -7.80633 | -4.87086 | 1.7877 |
| H | -7.86786 | -5.84703 | 0.32012 |
| H | -8.52983 | 4.21122 | -0.33105 |
| H | -7.80223 | 4.9381 | -1.77101 |
| H | -7.88248 | 5.85072 | -0.26404 |

Table S7. Structure of ***m-*2urea**, S0 [DFT/B3LYP/6-31G (d, p), *E*sp = -1836.90833149 hartree].

|  |  |  |  |
| --- | --- | --- | --- |
| atom | x[Å] | y[Å] | z[Å] |
| C | -1.62002 | -3.20337 | 2.54228 |
| C | -2.15578 | 4.48958 | -2.75003 |
| C | -2.06926 | 5.4232 | -1.74863 |
| C | -1.5207 | 5.08233 | -0.48447 |
| C | -1.06354 | 3.73803 | -0.22415 |
| C | -1.04869 | 2.81841 | -1.33748 |
| C | -1.429 | 6.08056 | 0.52102 |
| C | -0.93075 | 5.78174 | 1.76371 |
| C | -0.5784 | 4.45092 | 2.06331 |
| C | -0.66338 | 3.42791 | 1.12893 |
| C | -0.34812 | 1.49892 | -1.35114 |
| C | -0.44541 | 2.04753 | 1.65552 |
| C | 0.70645 | 1.74549 | 2.39668 |
| C | 0.86096 | 0.48022 | 2.96012 |
| C | -0.12049 | -0.49001 | 2.79172 |
| C | -1.28219 | -0.19632 | 2.05954 |
| C | -1.44707 | 1.07904 | 1.50574 |
| C | -1.01628 | 0.33415 | -1.7578 |
| C | -0.31473 | -0.86424 | -1.86705 |
| C | 1.04831 | -0.94409 | -1.58394 |
| C | 1.7228 | 0.2169 | -1.17843 |
| C | 1.02008 | 1.42576 | -1.07571 |
| O | 3.70943 | -1.96059 | -1.04623 |
| C | 10.17418 | -3.30011 | 0.24741 |
| C | 7.63939 | -0.4566 | -0.04735 |
| C | 8.83273 | -1.14929 | 0.12896 |
| C | 8.88558 | -2.5444 | 0.02508 |
| C | 7.69075 | -3.21137 | -0.26954 |
| C | 6.48338 | -2.5387 | -0.45065 |
| C | 6.44922 | -1.14081 | -0.33852 |
| N | 5.28283 | -0.36424 | -0.49866 |
| C | 4.00293 | -0.79282 | -0.82671 |
| N | 3.10087 | 0.25942 | -0.87685 |
| H | -1.59874 | 2.49937 | -3.36821 |
| H | -2.5872 | 4.74556 | -3.71307 |
| H | -2.42021 | 6.44001 | -1.90279 |
| H | -1.76626 | 7.08587 | 0.28334 |
| H | -0.85452 | 6.54651 | 2.53087 |
| H | -0.28836 | 4.19763 | 3.07832 |
| H | 1.48101 | 2.49672 | 2.51693 |
| H | 0.01384 | -1.47967 | 3.22272 |
| H | -2.08409 | 0.36449 | -1.9446 |
| H | -0.83923 | -1.76445 | -2.17509 |
| H | 1.58764 | -1.87614 | -1.66496 |
| H | 1.54751 | 2.32926 | -0.77864 |
| H | 7.63156 | 0.62848 | 0.03719 |
| H | 9.73921 | -0.5911 | 0.34965 |
| H | 7.69731 | -4.2946 | -0.36524 |
| H | 5.57618 | -3.07622 | -0.68449 |
| H | 5.43377 | 0.63 | -0.4128 |
| H | 3.42787 | 1.16804 | -0.58333 |
| H | 11.04569 | -2.69223 | -0.01451 |
| H | 10.2099 | -4.2146 | -0.35257 |
| H | 10.29001 | -3.59751 | 1.29756 |
| H | 1.75592 | 0.24159 | 3.52727 |
| H | -2.34944 | 1.30496 | 0.95809 |
| N | -2.24089 | -1.22377 | 1.94297 |
| C | -3.36916 | -1.25801 | 1.13339 |
| H | -1.99136 | -2.07329 | 2.42755 |
| N | -4.04059 | -2.46801 | 1.22865 |
| C | -5.21963 | -2.86781 | 0.56423 |
| H | -3.66451 | -3.16404 | 1.85537 |
| C | -5.69372 | -4.16216 | 0.8265 |
| C | -5.93461 | -2.05271 | -0.32551 |
| C | -6.85119 | -4.63233 | 0.21493 |
| H | -5.15364 | -4.80542 | 1.51866 |
| C | -7.57564 | -3.83543 | -0.67958 |
| H | -7.1958 | -5.63845 | 0.44044 |
| C | -7.09144 | -2.5457 | -0.92707 |
| H | -5.58415 | -1.05185 | -0.53043 |
| H | -7.63385 | -1.89724 | -1.61101 |
| C | -8.81403 | -4.35644 | -1.36937 |
| H | -9.32473 | -5.10952 | -0.76137 |
| H | -8.57061 | -4.82637 | -2.33086 |
| H | -9.52587 | -3.55113 | -1.57493 |
| O | -3.73464 | -0.32776 | 0.42672 |

Table S8. Structure of ***p-*1urea**, S0 [DFT/B3LYP/6-31G (d, p), *E*sp = -1111.41232386 hartree].

|  |  |  |  |
| --- | --- | --- | --- |
| atom | x[Å] | y[Å] | z[Å] |
| H | -0.42735 | 1.84713 | 1.82129 |
| H | -2.81227 | 1.30192 | 1.63949 |
| C | -0.73808 | 1.00883 | 1.20076 |
| H | -3.5658 | -2.75336 | 0.86683 |
| H | -5.92912 | -3.4946 | 0.80647 |
| C | -2.08938 | 0.70399 | 1.09336 |
| H | 1.70727 | 1.43218 | 1.28209 |
| C | -4.33525 | -2.05241 | 0.55721 |
| C | -5.68357 | -2.47242 | 0.53373 |
| H | 5.94793 | 2.02004 | 1.35623 |
| H | 3.78285 | 1.48259 | 1.13683 |
| N | 1.57524 | 0.62444 | 0.69146 |
| C | 0.2292 | 0.24253 | 0.53016 |
| C | -2.52958 | -0.37782 | 0.31316 |
| C | 6.21247 | 1.18211 | 0.71394 |
| N | 3.87172 | 0.67806 | 0.53397 |
| C | -3.96732 | -0.75671 | 0.23161 |
| C | -6.67673 | -1.58765 | 0.18795 |
| H | 8.30983 | 1.59526 | 0.83802 |
| C | 7.55014 | 0.9404 | 0.41865 |
| H | -7.7185 | -1.89718 | 0.18073 |
| C | 2.70866 | 0.02617 | 0.1535 |
| C | -0.19118 | -0.84383 | -0.25174 |
| C | 5.20324 | 0.36151 | 0.18812 |
| C | -1.55004 | -1.13585 | -0.34599 |
| C | -4.98625 | 0.17585 | -0.16935 |
| C | -6.35737 | -0.2526 | -0.17457 |
| H | 0.54232 | -1.439 | -0.7754 |
| O | 2.68054 | -0.95913 | -0.57105 |
| C | 7.9312 | -0.12461 | -0.40625 |
| H | -1.86082 | -1.97308 | -0.96413 |
| C | 5.56486 | -0.70797 | -0.64394 |
| C | -7.37057 | 0.66648 | -0.56012 |
| H | 9.81267 | -1.11073 | 0.02454 |
| C | -4.70023 | 1.5016 | -0.60056 |
| H | -8.40441 | 0.3308 | -0.55073 |
| C | 9.38499 | -0.40764 | -0.70158 |
| H | 9.98726 | 0.50518 | -0.66158 |
| C | 6.91171 | -0.93087 | -0.92569 |
| H | 4.797 | -1.34373 | -1.05959 |
| C | -7.05763 | 1.94857 | -0.94695 |
| C | -5.706 | 2.36407 | -0.97656 |
| H | 7.17199 | -1.76292 | -1.57556 |
| H | 9.51228 | -0.8513 | -1.69375 |
| H | -7.84276 | 2.63874 | -1.24153 |
| H | -5.45932 | 3.36907 | -1.3066 |
| H | -3.66783 | 1.82815 | -0.64639 |

Table S9. Structure of ***p-*2urea** with two equivalents of AcO–, S0 [DFT/CAM-B3LYP/6-31G+ (d), *E*sp = -2292.88700236 hartree].

|  |  |  |  |
| --- | --- | --- | --- |
| atom | x[Å] | y[Å] | z[Å] |
| C | 8.69305 | -5.54101 | 2.25067 |
| H | 8.33751 | -4.7094 | -0.33413 |
| C | 7.73418 | -4.50038 | 1.72593 |
| C | 7.67696 | -4.19334 | 0.36118 |
| C | 6.86911 | -3.81051 | 2.57053 |
| H | 6.88426 | -4.0229 | 3.63858 |
| C | 6.79907 | -3.24498 | -0.13774 |
| H | 6.77215 | -3.0179 | -1.20373 |
| C | 5.97474 | -2.85039 | 2.09709 |
| C | 5.92987 | -2.55852 | 0.72964 |
| H | 5.31383 | -2.32543 | 2.77276 |
| H | 5.13547 | -1.51748 | -0.88512 |
| N | 5.07308 | -1.62577 | 0.14428 |
| C | 4.19029 | -0.78386 | 0.77269 |
| O | 4.02889 | -0.71635 | 1.99098 |
| H | 3.75832 | -0.15214 | -1.12058 |
| N | 3.49904 | -0.00883 | -0.14133 |
| H | 2.50019 | 0.85855 | 2.2507 |
| C | 2.66453 | 1.07658 | 0.12002 |
| C | 2.22609 | 1.45902 | 1.39506 |
| H | -4.94359 | -2.26836 | 0.98171 |
| H | -6.15989 | -4.10475 | 1.41088 |
| H | -3.92 | -0.6184 | 1.13917 |
| C | 2.25125 | 1.84347 | -0.98096 |
| H | 2.56478 | 1.54543 | -1.97809 |
| C | 1.46897 | 2.61509 | 1.54921 |
| H | -3.1094 | 1.34486 | 1.87421 |
| C | -6.16195 | -4.37052 | 0.35686 |
| H | 1.15521 | 2.89894 | 2.55084 |
| H | -7.3241 | -6.13718 | 0.65986 |
| C | -2.76976 | 1.60109 | 0.87152 |
| N | -3.66598 | -0.48669 | 0.14625 |
| N | -4.85821 | -2.41351 | -0.02993 |
| C | -6.81483 | -5.5142 | -0.07389 |
| H | -2.02982 | 3.51665 | 1.44827 |
| C | -2.16551 | 2.822 | 0.62371 |
| C | 1.4878 | 2.9853 | -0.80833 |
| C | -3.0026 | 0.69964 | -0.17949 |
| C | -5.48617 | -3.53746 | -0.55234 |
| C | 1.10408 | 3.41842 | 0.46645 |
| C | -4.1534 | -1.43789 | -0.71247 |
| C | -1.78459 | 3.20251 | -0.66988 |
| C | -2.57503 | 1.03956 | -1.46909 |
| C | -6.82839 | -5.88407 | -1.42248 |
| H | 1.21998 | 3.57757 | -1.67887 |
| O | -3.9975 | -1.43657 | -1.93356 |
| C | -5.49014 | -3.898 | -1.90601 |
| C | -1.98778 | 2.27993 | -1.697 |
| C | 0.5611 | 4.79164 | 0.65295 |
| C | -1.4177 | 4.61816 | -0.94614 |
| C | -7.55533 | -7.12245 | -1.88596 |
| H | -2.72376 | 0.34102 | -2.28036 |
| C | -6.1531 | -5.0535 | -2.31414 |
| H | 2.02768 | 5.16733 | 2.1443 |
| C | -0.46974 | 5.37432 | -0.16837 |
| H | -2.91059 | 4.71055 | -2.45452 |
| C | -2.18722 | 5.28341 | -1.88249 |
| C | 1.24082 | 5.60663 | 1.53912 |
| H | -4.97119 | -3.27172 | -2.61795 |
| H | -1.68026 | 2.53276 | -2.70927 |
| C | -2.14702 | 6.68359 | -2.03376 |
| C | -0.55722 | 6.8021 | -0.21541 |
| C | 1.02785 | 6.99794 | 1.5998 |
| H | -6.13542 | -5.31223 | -3.37159 |
| C | -1.38983 | 7.43296 | -1.17546 |
| H | -2.77642 | 7.16229 | -2.77972 |
| C | 0.18773 | 7.5916 | 0.6982 |
| H | 1.59014 | 7.59706 | 2.31148 |
| H | -1.41131 | 8.5198 | -1.21145 |
| H | 0.0745 | 8.67279 | 0.66451 |
| H | 8.48931 | -6.5324 | 1.82599 |
| H | 8.62149 | -5.62886 | 3.34034 |
| H | 9.73429 | -5.29466 | 2.00632 |
| H | -7.29262 | -7.99732 | -1.27898 |
| H | -7.30943 | -7.35676 | -2.92719 |
| H | -8.64519 | -7.00301 | -1.82546 |
| C | 5.50284 | -1.34043 | -3.45705 |
| O | 4.79753 | -0.86009 | -2.51249 |
| C | 5.17347 | -0.80704 | -4.85555 |
| O | 6.41136 | -2.18572 | -3.33797 |
| O | -4.38891 | 0.46065 | 3.66132 |
| H | 5.26703 | 0.28444 | -4.86662 |
| H | 4.1323 | -1.04355 | -5.10108 |
| H | 5.83574 | -1.24274 | -5.60803 |
| C | -5.52053 | -1.30292 | 4.81944 |
| C | -4.82826 | -0.70122 | 3.59045 |
| H | -5.56378 | -0.57998 | 5.63791 |
| H | -4.97444 | -2.19492 | 5.1461 |
| H | -6.53443 | -1.62293 | 4.554 |
| O | -4.75639 | -1.47003 | 2.57684 |

Table S10. Structure of ***m-*2urea** with two equivalents of AcO–, S0 [DFT/CAM-B3LYP/6-31G+ (d), *E*sp = -2292.89572959 hartree].

|  |  |  |  |
| --- | --- | --- | --- |
| atom | x[Å] | y[Å] | z[Å] |
| C | 1.9452 | 4.48262 | -1.11213 |
| C | 1.8771 | 5.88601 | -1.0555 |
| C | 0.75293 | 6.47609 | -0.55436 |
| C | -0.3107 | 5.68874 | -0.04529 |
| C | -0.2243 | 4.25405 | -0.02261 |
| C | 0.93821 | 3.65958 | -0.6425 |
| C | -1.46224 | 6.35796 | 0.44029 |
| C | -2.51076 | 5.65191 | 0.95587 |
| C | -2.41143 | 4.25297 | 1.05424 |
| C | -1.30891 | 3.54331 | 0.61513 |
| C | 1.15158 | 2.20621 | -0.91568 |
| C | -1.34637 | 2.08432 | 0.93822 |
| C | -0.33809 | 1.47845 | 1.68644 |
| C | -0.47836 | 0.14742 | 2.06858 |
| C | -1.61483 | -0.57457 | 1.73613 |
| C | -2.64637 | 0.02837 | 1.00094 |
| C | -2.49303 | 1.35871 | 0.59681 |
| C | 0.22915 | 1.44914 | -1.64215 |
| C | 0.53908 | 0.13695 | -1.97719 |
| C | 1.75414 | -0.4454 | -1.62647 |
| C | 2.69331 | 0.30979 | -0.9138 |
| C | 2.36882 | 1.62727 | -0.56115 |
| O | 4.00949 | -2.25209 | -1.46998 |
| C | 9.84178 | -5.49594 | -0.69922 |
| C | 8.05137 | -2.20805 | 0.03983 |
| C | 9.02257 | -3.19315 | -0.03266 |
| C | 8.77213 | -4.43356 | -0.63144 |
| C | 7.49983 | -4.64171 | -1.15629 |
| C | 6.50204 | -3.66867 | -1.0982 |
| C | 6.77007 | -2.4354 | -0.49458 |
| N | 5.85092 | -1.39247 | -0.37482 |
| C | 4.56101 | -1.34718 | -0.84388 |
| N | 3.95394 | -0.1479 | -0.52424 |
| H | 2.8059 | 4.01794 | -1.58143 |
| H | 2.69943 | 6.48275 | -1.44066 |
| H | 0.64871 | 7.55843 | -0.53483 |
| H | -1.488 | 7.44398 | 0.38894 |
| H | -3.40112 | 6.15695 | 1.3205 |
| H | -3.21586 | 3.70106 | 1.52862 |
| H | 0.54999 | 2.03648 | 1.96396 |
| H | -1.718 | -1.61204 | 2.04297 |
| H | -0.72209 | 1.88029 | -1.93607 |
| H | -0.18594 | -0.45642 | -2.52785 |
| H | 1.98648 | -1.4658 | -1.89585 |
| H | 3.0941 | 2.20593 | 0.00565 |
| H | 8.26708 | -1.24775 | 0.5086 |
| H | 10.00527 | -2.98889 | 0.38998 |
| H | 7.26753 | -5.59466 | -1.62943 |
| H | 5.52119 | -3.85267 | -1.51411 |
| H | 6.18051 | -0.53505 | 0.10491 |
| H | 4.54056 | 0.5202 | -0.01853 |
| H | 10.72803 | -5.14658 | -1.24428 |
| H | 9.47395 | -6.39346 | -1.20839 |
| H | 10.17823 | -5.79844 | 0.30071 |
| H | 0.31247 | -0.33522 | 2.63595 |
| H | -3.27928 | 1.81796 | 0.01464 |
| N | -3.77335 | -0.75081 | 0.72791 |
| C | -4.94896 | -0.36182 | 0.11557 |
| H | -3.76857 | -1.7022 | 1.10428 |
| N | -5.87784 | -1.37179 | 0.12635 |
| C | -7.16754 | -1.35379 | -0.40675 |
| H | -5.58388 | -2.2413 | 0.6097 |
| C | -7.93872 | -2.51625 | -0.2248 |
| C | -7.72967 | -0.27563 | -1.09894 |
| C | -9.22788 | -2.58409 | -0.727 |
| H | -7.50702 | -3.35814 | 0.31709 |
| C | -9.80612 | -1.51616 | -1.42362 |
| H | -9.80071 | -3.49709 | -0.571 |
| C | -9.03045 | -0.37309 | -1.59358 |
| H | -7.14693 | 0.62363 | -1.24187 |
| H | -9.44618 | 0.47854 | -2.13029 |
| C | -11.21158 | -1.60914 | -1.9653 |
| H | -11.94359 | -1.79038 | -1.16788 |
| H | -11.31514 | -2.42821 | -2.68844 |
| H | -11.50014 | -0.68249 | -2.47352 |
| O | -5.13282 | 0.75345 | -0.3752 |
| C | 7.2053 | 1.55451 | 1.2844 |
| O | 8.27582 | 0.92122 | 1.36356 |
| O | 6.12185 | 1.13199 | 0.76622 |
| C | 7.14825 | 2.97677 | 1.8524 |
| H | 6.86613 | 3.67892 | 1.06013 |
| H | 8.11206 | 3.26862 | 2.27717 |
| H | 6.37242 | 3.03404 | 2.62366 |
| H | -3.8571 | -4.99031 | 3.52869 |
| C | -4.17706 | -5.45104 | 2.58764 |
| H | -4.70621 | -6.38438 | 2.7957 |
| H | -3.2714 | -5.66113 | 2.0085 |
| C | -5.06768 | -4.47456 | 1.81337 |
| O | -4.52958 | -3.35659 | 1.52747 |
| O | -6.22793 | -4.82474 | 1.5208 |

Table S11. Structure of ***p-*1urea** with one equivalent of AcO–, S0 [DFT/CAM-B3LYP/6-31G+ (d), *E*sp = -1339.32176345 hartree].

|  |  |  |  |
| --- | --- | --- | --- |
| atom | x[Å] | y[Å] | z[Å] |
| H | 0.65889 | 1.9352 | -0.62529 |
| H | 3.08651 | 1.54084 | -0.7598 |
| C | 1.05782 | 0.93254 | -0.50058 |
| H | 4.12473 | -2.25694 | -2.11469 |
| H | 6.53226 | -2.76271 | -2.41234 |
| C | 2.42108 | 0.70269 | -0.56803 |
| H | -1.39357 | 1.2153 | -0.33923 |
| C | 4.85521 | -1.76322 | -1.48066 |
| C | 6.22764 | -2.04358 | -1.65663 |
| H | -5.62526 | 1.37672 | -0.0386 |
| H | -3.45894 | 1.02711 | -0.15634 |
| N | -1.19152 | 0.2024 | -0.2158 |
| C | 0.1586 | -0.12712 | -0.27518 |
| C | 2.9546 | -0.58529 | -0.42182 |
| C | -5.8167 | 0.31891 | 0.11802 |
| N | -3.45699 | -0.00243 | -0.0182 |
| C | 4.41128 | -0.85191 | -0.54533 |
| C | 7.16773 | -1.3998 | -0.89714 |
| H | -7.93372 | 0.56227 | 0.24575 |
| C | -7.11032 | -0.14952 | 0.27888 |
| H | 8.22794 | -1.5977 | -1.03542 |
| C | -2.251 | -0.65795 | -0.02126 |
| C | 0.67982 | -1.42107 | -0.12848 |
| C | -4.724 | -0.5662 | 0.15397 |
| C | 2.05291 | -1.62988 | -0.20779 |
| C | 5.38111 | -0.19445 | 0.28525 |
| C | 6.76768 | -0.46518 | 0.09171 |
| H | 0.00344 | -2.24496 | 0.04793 |
| O | -2.12553 | -1.87495 | 0.13212 |
| C | -7.38028 | -1.5074 | 0.48158 |
| H | 2.43447 | -2.64063 | -0.08214 |
| C | -4.97824 | -1.92742 | 0.35605 |
| C | 7.72444 | 0.19475 | 0.90772 |
| H | -9.41461 | -1.7775 | -0.22095 |
| C | 5.01321 | 0.70021 | 1.32714 |
| H | 8.77879 | -0.01435 | 0.74169 |
| C | -8.79439 | -2.00373 | 0.65539 |
| H | -9.28272 | -1.54276 | 1.52307 |
| C | -6.29037 | -2.37239 | 0.51514 |
| H | -4.15048 | -2.62129 | 0.3864 |
| C | 7.33566 | 1.06888 | 1.88842 |
| C | 5.9606 | 1.31499 | 2.10555 |
| H | -6.46032 | -3.43648 | 0.67092 |
| H | -8.81587 | -3.08865 | 0.80303 |
| H | 8.07914 | 1.56498 | 2.50638 |
| H | 5.65192 | 1.99106 | 2.89781 |
| H | 3.96094 | 0.88495 | 1.50881 |
| O | -1.48041 | 2.95965 | -0.57255 |
| C | -2.64847 | 3.43553 | -0.54725 |
| C | -2.77717 | 4.94478 | -0.74752 |
| H | -2.18794 | 5.46666 | 0.01383 |
| H | -3.82041 | 5.26349 | -0.69037 |
| H | -2.36094 | 5.2194 | -1.72268 |
| O | -3.70475 | 2.77194 | -0.37368 |

1. **Supplementary References**

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