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S U P P O R T I N G I N F O R M A T I O N

Synthesis and Characterization of Oligoproline Based Molecular Assemblies for Light Harvesting

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This compound was synthesized based on literature methods.[1] All steps were carried out in low ambient light conditions with aluminum foil-shielded glassware. Boc-Pra-OCH_3·HCl (1.12 g, 4.0 mmol, 280 g/mol), NMM (1.3 g, 13.2 mmol, 101 g/mol), DCC (0.846 g, 4.4 mmol, 206.3 g/mol), and DMAP (0.049 g, 0.4 mmol, 122 g/mol) and PTZ$(CH_2)_2$COOH (1.08g, 4.0 mmol, 271 g/mol) were combined in a 150 mL round bottomed flask. Methylene chloride (75 mL) was added and a septum was used to seal the flask. After stirring the mixture for 22 hours four drops of acetic acid were added and the mixture was stirred for an additional hour. Solid dicyclohexyl urea, that formed over the course of the reaction, was removed by vacuum filtration and the solvent was removed under reduced pressure to yield a red oil. Ethyl acetate was added to the oil causing precipitation of a white solid, which dissolved upon gentle heating. The mixture was chromatographed on silica gel and was eluted with a 1:1 (v/v) ethyl acetate/hexanes solution. After elution of the first band the mobile phase was switched to 100 % ethyl acetate to remove the product. The solvent was removed under reduced pressure to yield a thin film that was dried in a vacuum dessicator for 12 hours (yield: 0.137 g, 69%). ^{1}H-NMR (200 MHz, CD_2Cl_2) δ 7.20 (m, 4H), 7.0 (m, 4H), 6.65 (m, 1H), 4.5 (m, 1H), 4.2 (m, 3H), 3.67 (s, 3H), 3.58 (m, 1H), 3.35 (m, 1H), 2.60 (t, 2H), 2.39 (m, 1H), 1.84 (m, 1H), and 1.49 ppm (d, 9H).

B. (*2S,4S*)-N^{α}-(1,1-Dimethylethoxycarbonyl)-4-(3-(*10H*-phenothiazine-10)propanoyl)-L-proline, Boc-Pra(PTZ)-OH, (**S2**)

All steps were carried out in low ambient light conditions. Aluminum foil was used to shield the reaction from light. Lithium hydroxide (0.100 g, 4 mmol, 23.9 g/mol) and Boc-Pra(PTZ)-OCH_3 (**S1**, 0.408 g, 0.8 mmol, 497.6 g/mol) were added to a 50 mL round bottomed flask that was submerged in an ice bath. A mixture of 3:1 (v/v) methanol/water (15 mL) was added and the flask was sealed with a septum. The mixture was stirred overnight, while gradually warming to room temperature. Methanol was removed by rotary evaporation and water

[1] McCafferty, D. G.; Bishop, B. M.; Wall, C. G.; Hughes, S. G.; Mecklenburg, S. L.; Meyer, T. J.; Erickson, B. W. *Tetrahedron* **1995**, *51*, 1093-1106.

(5 mL) was added to the flask. The pH of the solution was adjusted to 2 with 0.1 M HCl causing the precipitation of a white solid that was extracted into ethyl acetate (3 × 40 mL) and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure to give a white solid (yield: 0.336 g, 87%). ^{1}H-NMR (200 MHz, CD_2Cl_2) δ 7.18 (m, 4H), 6.95 (m, 4H), 6.43 (m, 1H), 4.37 (m, 2H), 4.18 (t, 2H), 3.5 (q, 1H), 3.35 (d, 1H), 2.58 (t, 2H), 2.23 (m, 2H), and 1.49 ppm (d, 9H).

II. Synthesis of the ruthenium chromophore, bis-(4,4'-diethylamidocarbonyl-2,2'-bipyridine)(4'-methyl-2,2'-bipyridine-4-carboxylic acid)ruthenium(II) ([Rub'$_2$m](PF$_6$)$_2$).

A. 4-Methyl-2,2'-bipyridine-4'-carboxaldehyde(**S3**)

This compound was made based on literature procedures.[2] Dioxane (200 mL) was added to 4,4'-dimethyl-2,2'-bipyridine (5.006 g, 27.17 mmol, 184.24 g/mol) in a 500 mL round bottomed flask and the solution was sparged with argon for 15 minutes by submerging a piece of teflon tubing in the flask and bubbling argon into the dioxane with stirring. Selenium dioxide (extremely toxic) (3.397 g, 30.62 mmol, 110.96 g/mol) was added to the flask and the argon sparging was continued for an additional 20 minutes. The solution was then heated at a gentle reflux for 24 hours and as the reaction progressed, solid selenium metal precipitated on the sides of the flask. After the solution cooled to room temperature it was gravity filtered and the solvent was removed under reduced pressure. The remaining solid was dissolved in ethyl acetate, heated at reflux for one hour and gravity filtered while hot. Next, the filtrate was washed with 0.1 M sodium carbonate (2 × 125 mL) to extract any acid bipyridine formed and then extracted into a solution of 0.3 M sodium metabisulfite. After using solid sodium bicarbonate to adjust the pH to approximately 10, the product was extracted into methylene chloride. Additional sodium carbonate was added to the aqueous solution to maximize partitioning into the organic layer. The solvent layers were separated and the organic solvent was removed under reduced pressure (yield: 2.42 g, 45%). ^{1}H-NMR (200 MHz, CD_2Cl_2) δ 10.13 (s, 1H), 8.82 (d, 1H), 8.80 (s, 1H), 8.54 (s, 1H), 8.27 (d, 1H), 7.67 (s, 1H), 7.20 (d, 1H), and 1.98 ppm (s, 3H).

[2] Peek, B. M.; Ross, G. T.; Edwards, S. W.; Meyer, G. J.; Meyer, T. J. Erickson, B. W. *Int. J. Pep. Protein Res*. **1991**, *38*, 114-123.

B. 4-Methyl-2,2'-bipyridine-4'-carboxylic acid (bpy-monoacid, **m**)

This compound was made according to literature procedures.[2] To a 300 mL round bottomed flask containing 95% (v/v) ethanol/water solution (80 mL) and **S3** (1.58 g, 8.00 mmol, 198.22 g/mol) was added an aqueous solution (20 mL) of silver nitrate (1.43 g, 8.40 mmol, 169.88 g/mol). Sodium hydroxide (1.0 M) was added via an addition funnel over 20 minutes and the solution was stirred for 24 hours. After stirring the black reaction mixture for 24 hours, the ethanol was removed under reduced pressure and the insoluble silver oxide was removed by filtration. The filtered solids were washed with aqueous 2.0 M sodium hydroxide (5 × 50 mL) and with water (2 × 100 mL). The combined aqueous filtrate was extracted with methylene chloride (2 × 250 mL) and the pH of the aqueous layer was adjusted to 3. Lowering the pH resulted in the formation of a white precipitate that was collected on a medium porosity fritted glass funnel and dried in a vacuum dessicator (yield: 76 %). ^{1}H-NMR. (250 MHz, $(CD_3)_2SO$) δ 8.83 (d, 1H), 8.79 (s, 1H), 8.55 (d, 1H), 8.24 (s, 1H), 7.84 (dd, 1H), 7.30 (dd, 1H), and 2.40 ppm (s, 3H).

C. 4,4'-diacylchloro-2,2'-bipyridine (bpy-diacidchloride, **S4**)

This compound was also synthesized according to literature procedures.[3] To a 500 mL oven-dried round bottomed flask was added 4,4'-dicarboxylic acid-2,2'-bipyridine (3.55 g, 14.5 mmol, 244.21 g/mol).[4] After purging the flask for 15 minutes with argon, thionyl chloride (200 mL) was carefully added and the heterogenous solution was stirred under argon for 10 minutes. The solution was then heated at reflux under a positive pressure of argon. After ~20 hours, the solution was cooled to room temperature and the liquid was decanted from a green film that lined the flask. The solvent was removed under reduced pressure and the solid was placed in a vacuum dessicator for 2 hours in preparation for conversion to the amide.

[3] Lutzen, A.; Hass, O.; Bruhn, T. *Tet. Lett*. **2002**, *43*, 1807-1811. Uppadine, L.; Redman, J. E.; Dent, S. W.; Drew, M. G. B.; Beer, P. D. *Inorg. Chem.* **2001**, *40*, 2860-2869.
[4] Launikonis, A.; Lay, P. A.; Mau, A. W. H.; Sargeson, A. M.; Sasse, W. H. F. *Aust. J. Chem*. **1986**, *39*, 1063.

D. 4,4'-diethylamidocarbonyl-2,2'-bipyridine (**b'**)

The synthesis of this ligand is based on literature procedures.[5] The flask containing **S4** (from the previous synthesis) was flushed with argon for 5 minutes and methylene chloride (60 mL) was added to it. An addition funnel was attached to the flask while maintaining the argon flow to the system. Diethylamine (25 mL), was added to the flask via the addition funnel over 20 minutes and the reaction was stirred at room temperature for one hour. Removal of the solvent under reduced pressure resulted in an oily brown residue which was dissolved in methylene chloride and chromatographed on neutral alumina with 5% (v/v) methanol in methylene chloride. The product eluted as a dark brown band from which the solvent was removed to yield an oil. This oil was dissolved in hot acetonitrile and added dropwise to vigorously stirring diethylether to produce a precipitate of protonated diethylamine, as shown by ^{1}H-NMR. The precipitate was removed by filtration and the solvent was removed under reduced pressure to yield a yellow oil. A 1:1 (v/v) mixture of ether/hexanes was added to give an emulsion and the solvent was again removed by rotary evaporation to yield small yellow-brown crystals (yield: 2.77 g, 54%). ^{1}H-NMR (200 MHz, $CDCl_3$) δ 8.72 (dd, 2H), 8.41 (d, 2H), 7.31 (dd, 2H), 3.59 (q, 4H), 3.28 (q, 4H), 1.28 (t, 6H), and 1.14 ppm (t, 6H).

E. *cis*-Dichloro-bis-(4,4'-diethylamidocarbonyl-2,2'-bipyridine) ruthenium(II) (**Rub'$_2$Cl$_2$**)

Ruthenium trichloride trihydrate (0.442 g, 1.69 mmol, 261.43 g/mol), **b'** (1.20 g, 3.38 mmol, 354.48 g/mol), lithium chloride (0.466 g, 11.0 mmol, 42.39 g/mol) and hydroquinone (0.149 g, 1.35 mmol, 110.11 g/mol) were combined in a 200 mL round bottomed flask to which DMF (35 mL) was added. The mixture was stirred for 5 minutes at room temperature and then heated at reflux for 2 hours. Progress of the reaction was monitored by UV-Vis spectrometry and showed MLCT bands at 394 and 568 nm grew in over the course of the reaction. After two hours, no change in the absorbance intensity of these two bands was observed relative to the other UV absorbance bands, and the reaction mixture was cooled to room temperature. The solvent was removed under reduced pressure and the dark sticky solid was dissolved in water (500 mL) with sonication and then extracted into methylene chloride (10 × 400 mL). The organic phase was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The

[5] Smith, G. D.; Maxwell, K. A.; DeSimone, J. M.; Meyer, T. J.; Palmer, R. A. *Inorg. Chem.* **2000**, *39*, 893-898.

sticky product was dissolved in a minimum of methylene chloride and added dropwise to vigorously stirring diethyl ether. This mixture was stirred overnight to yield dark violet crystals of Rud_2Cl_2 which were collected on a medium porosity fritted glass funnel (yield: 1.47 g, 95%). ^{1}H-NMR (200 MHz, CD_2Cl_2) δ 10.20 (d, 2H), 8.23 (s, 2H), 8.05 (s, 2H), 7.53 (m, 4H), 6.91 (m, 2H), 3.4 (m, 16H), and 1.2 ppm (m, 24 H).

F. Bis-(4,4'-diethylamidocarbonyl-2,2'-bipyridine)(4'-methyl-2,2'-bipyridine-4-carboxylic acid)ruthenium(II), **[Rub'$_2$m](PF$_6$)$_2$**

To a 100 mL round bottomed flask containing Rud_2Cl_2 (1.356 g, 1.48 mmol, 916.64 g/mol) and bpy-monoacid, **m**, (0.380 g, 1.77 mmol, 214.22g/mol) was added 70% (v/v) ethanol in water. After heating the solution at reflux for approximately 24 hours the ethanol was removed under reduced pressure and water (30 mL) was added. The solution was filtered to remove unreacted **m** and 1 M hexafluorophosphoric acid was added to precipitate the product, which was collected on a medium porosity fritted glass funnel, and washed with water (2 × 5 mL) then washed with diethyl ether (5 × 100 mL) (yield: 1.65 g, 85 %). ^{1}H-NMR (200 MHz, CD_3CN) δ 8.9 (d, 1H), 8.45 (m, 4H), 7.91 (m, 1H), 7.80 (m, 3H), 7.70 (m, 2H), 7.60 (m, 1H), 7.30 (m, 6H) 3.49 (m, 8H), 3.21 (m, 8H), 2.55 (s, 3H), 1.20 (t, 12H), and 1.02 ppm (t, 12H).

III. Synthesis of arrays 7, 8 and 9

B. CH_3-CO-Pro_6-Pra(PTZ)-Pro_3-Pra($Ru^{II}b'_2m)^{2+}$-Pro_6-NH_2 (**7**)

Manual solid phase peptide synthesis was employed to assemble **7** in the same manner as **6** (see Main text). The desalted peptide was purified by semi-preparative reversed-phase HPLC on an octadecyl-silica column (C18) eluted over 60 minutes with a linear gradient of 14 % to 42 % acetonitrile in 0.06% TFA/water. Fractions containing the desired peptide were freed of solvent by evaporation under reduced pressure and lyophilization to yield **7** as a flocculent orange powder (yield: 0.060 mg). ESI-MS (calcd for $[C_{154}H_{197}N_{31}O_{24}SRu]^{2+}$: 2999.59 Da) 3000 Da.

C. CH_3-CO-Pro_6-Pra(PTZ)-Pro_4-Pra($Ru^{II}b'_2m)^{2+}$-Pro_6-NH_2 (**8**)

Manual solid phase peptide synthesis was employed to assemble the 18-residue peptide in the same manner as **6**. The desalted peptide was purified by semi-preparative reversed-phase HPLC as described for **6** (yield: 0.060 g). ESI-MS (calcd for $[C_{159}H_{204}N_{32}O_{25}SRu]^{2+}$: 3096.7 Da) 3096 Da.

D. CH_3-CO-Pro_6-Pra(PTZ)-Pro_5-Pra($Ru^{II}b'_2)^{2+}$-Pro_6-NH_2 (**9**)

Manual solid phase peptide synthesis was employed to assemble the 19-residue peptide in the same manner as **6**. The desalted peptide was purified by semi-preparative reversed-phase HPLC as described for **6** (yield: 0.055 g). ESI-MS (calcd for $[C_{164}H_{211}N_{33}O_{26}SRu]^{2+}$: 3193.82 Da) 3194 Da

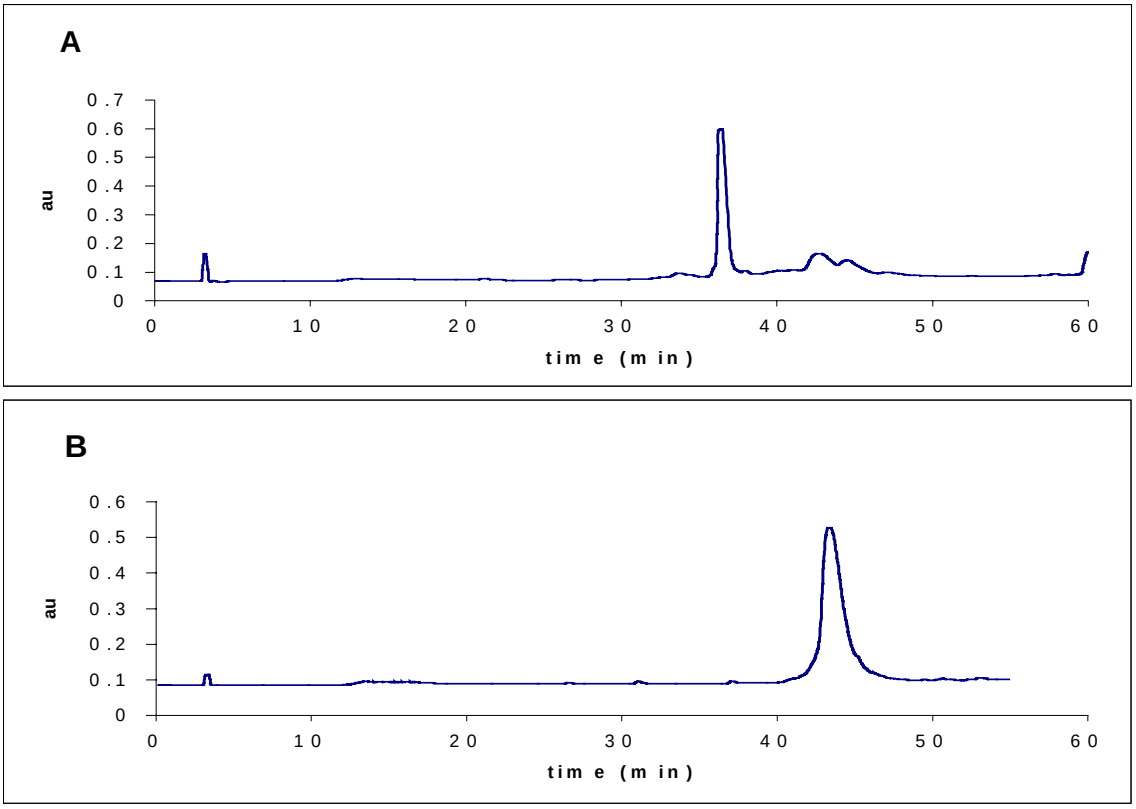

Figure S1. A) Analytical HPLC chromatogram of 6 before (A) and after (B) semi-preparative HPLC purification.

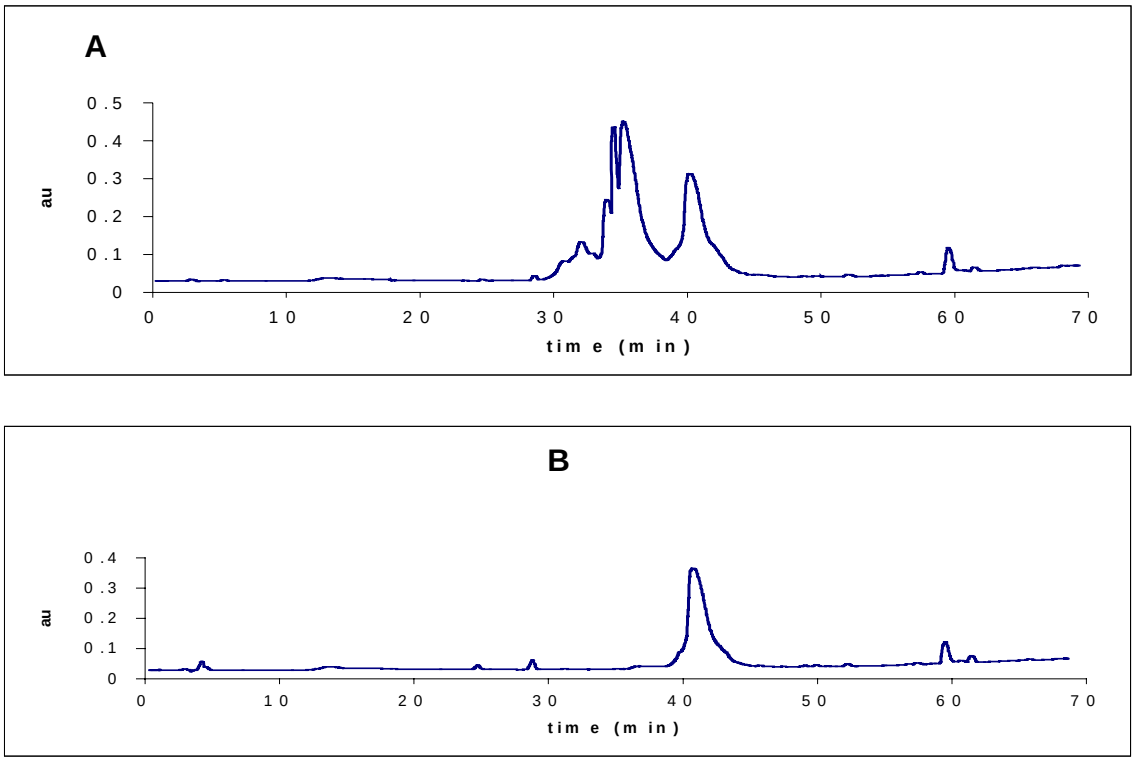

Figure S2. A) Analytical HPLC chromatogram of **7** before (A) and after (B) semi-preparative HPLC purification.

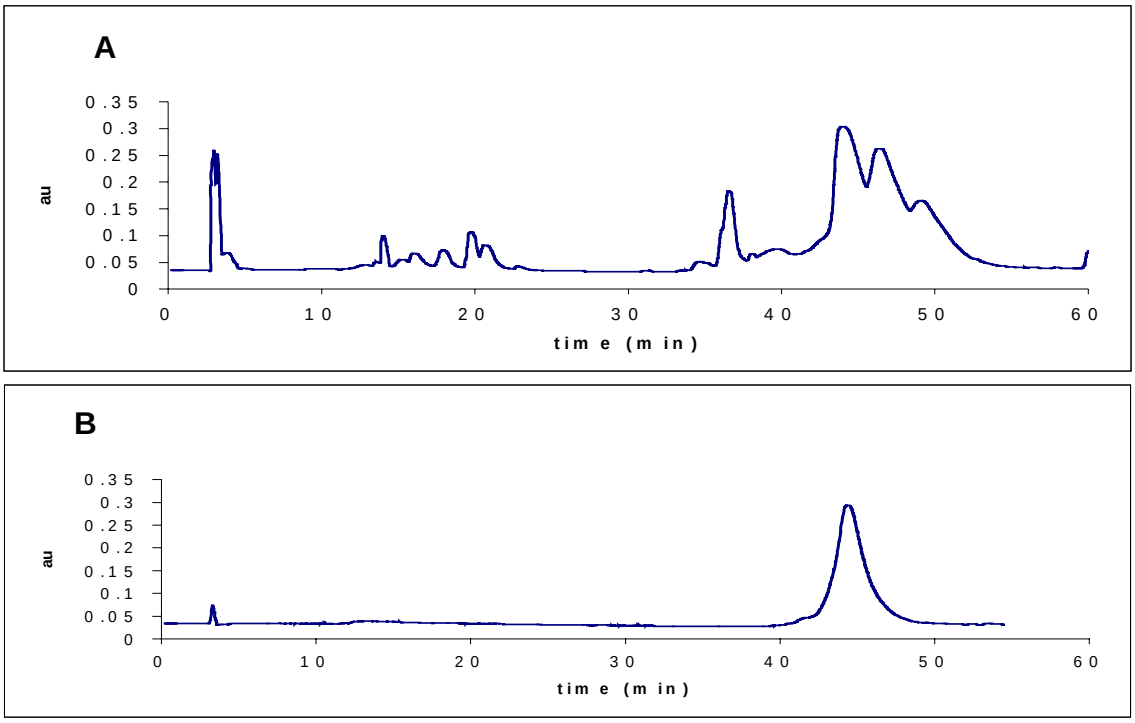

Figure S3. A) Analytical HPLC chromatogram of **8** before (A) and after (B) semi-preparative HPLC purification.

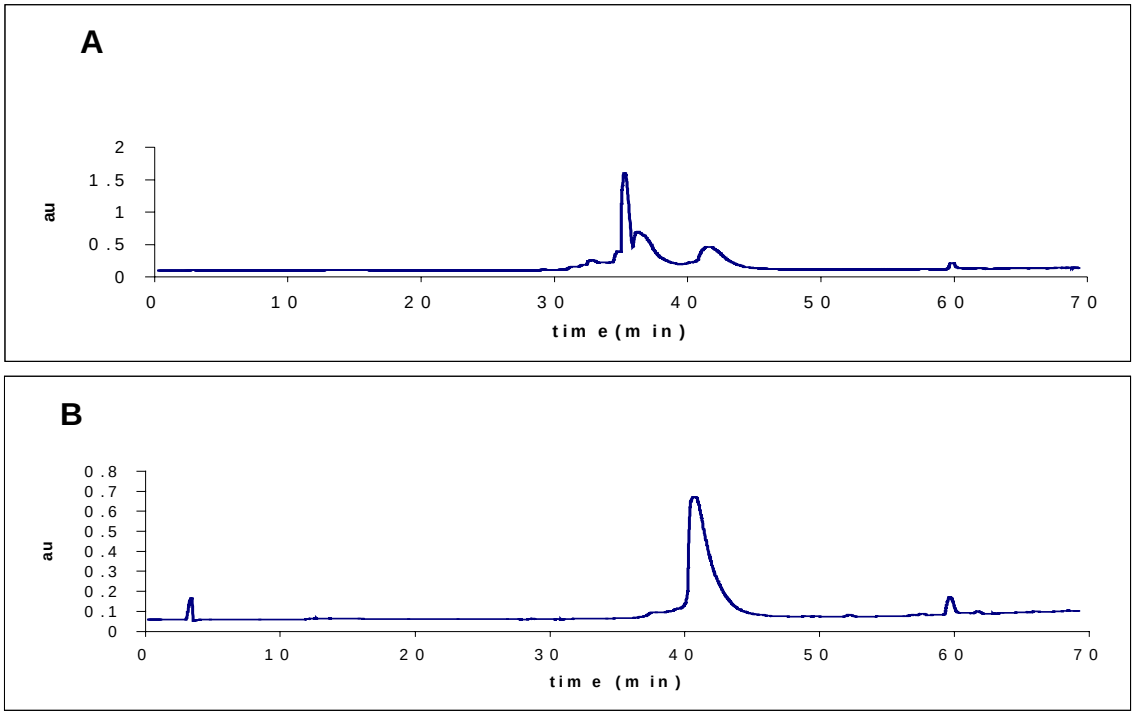

Figure S4. A) Analytical HPLC chromatogram of **9** before (A) and after (B) semi-preparative HPLC purification.

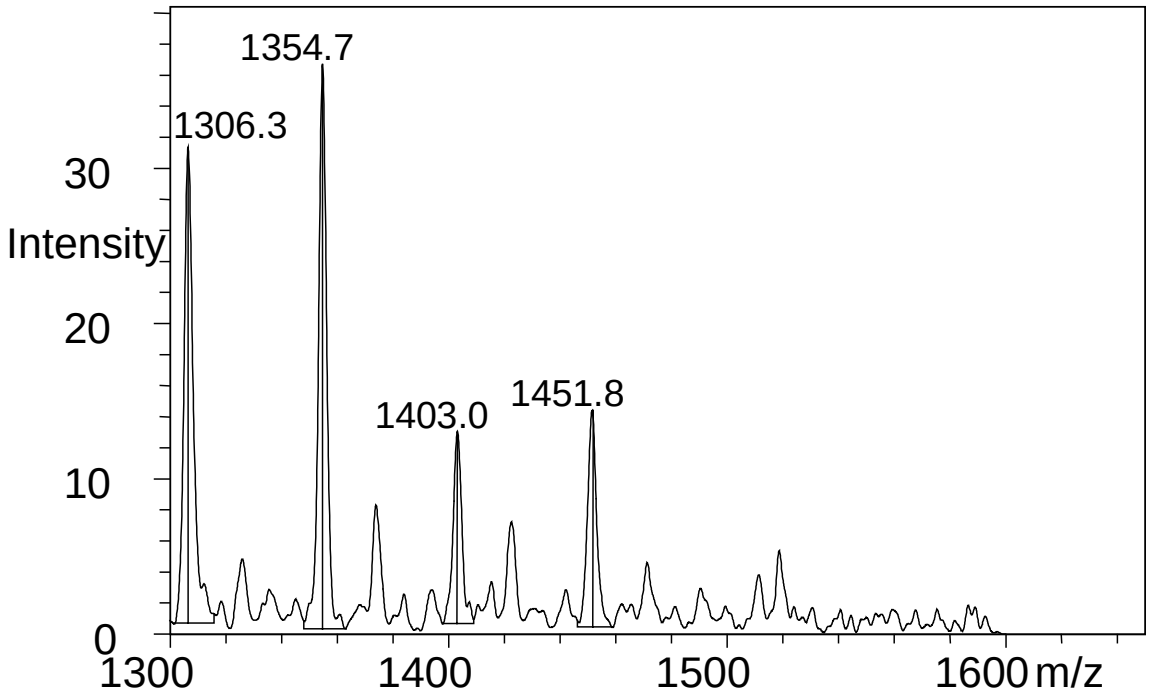

Figure S5. ESI mass spectrum of **6** (2904 Da) measured after purification.

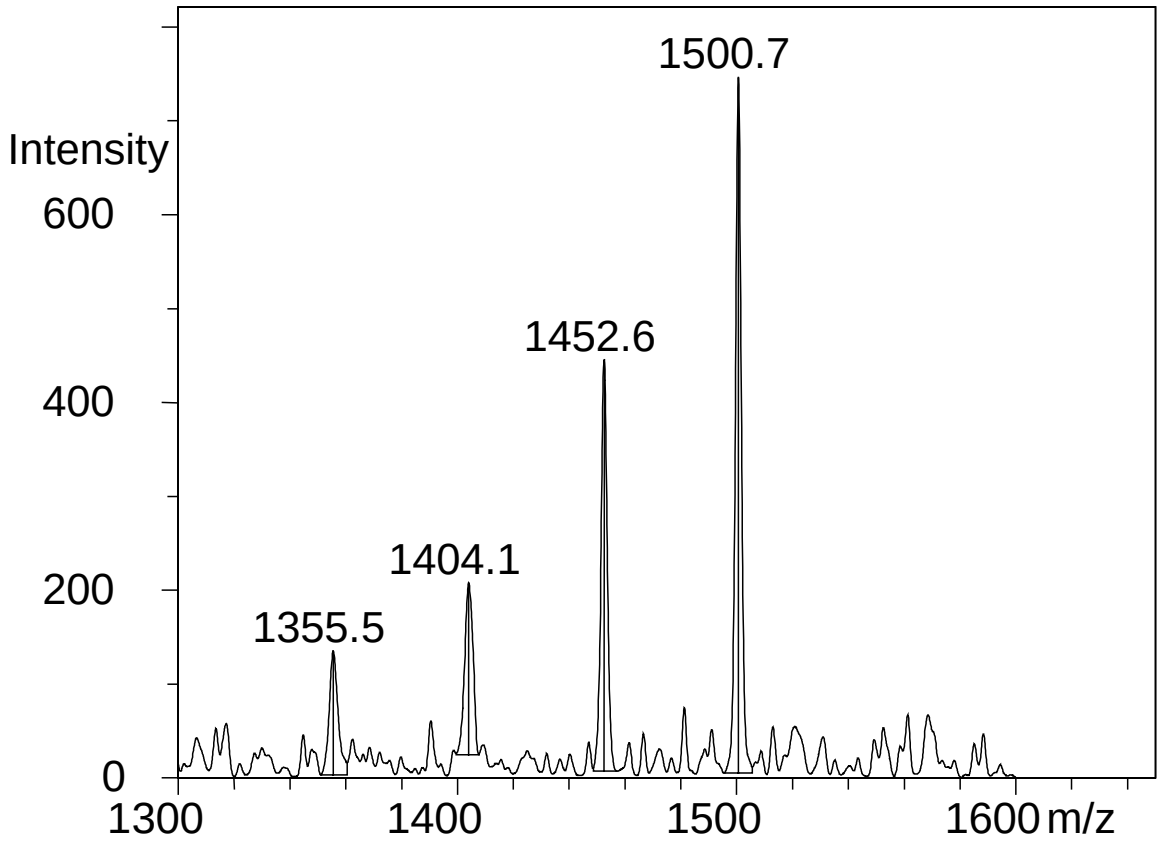

Figure S6. ESI mass spectrum of **7** (3000 Da) measured after purification**.**

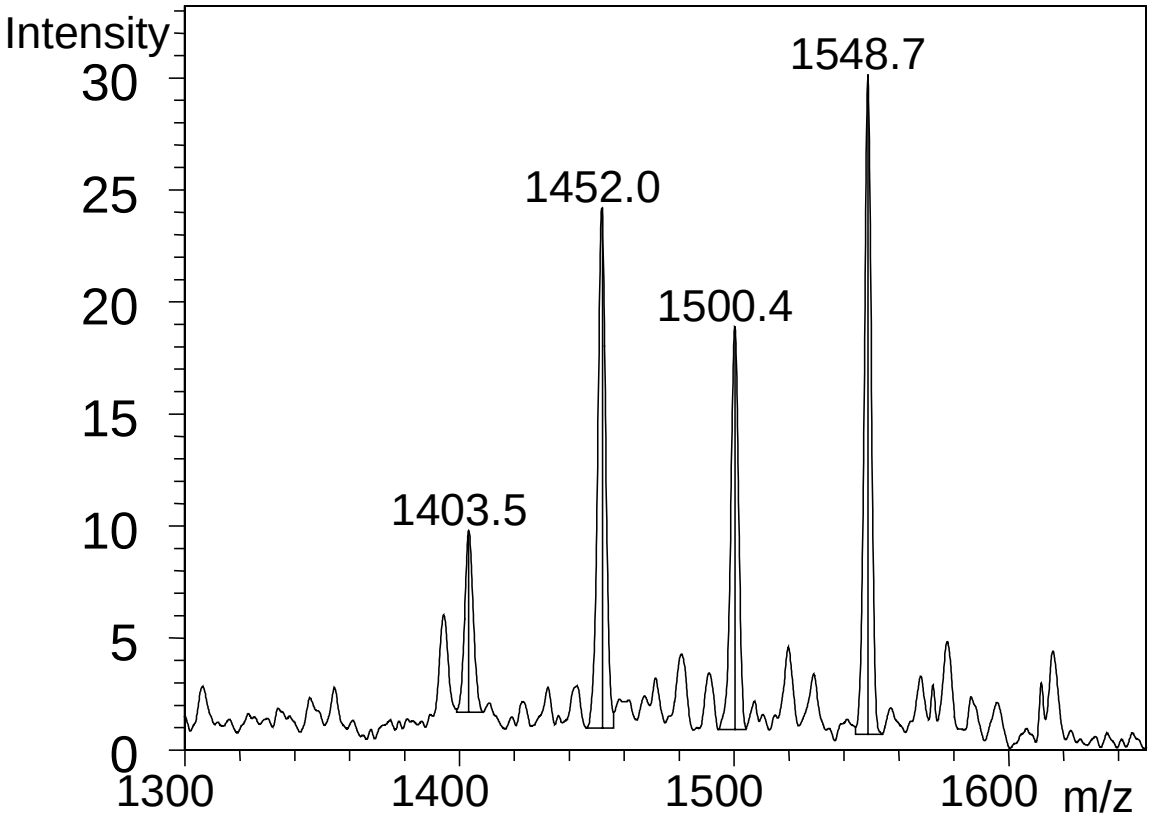

Figure S7. ESI mass spectrum of **8** (3096 Da) measured after purification**.**

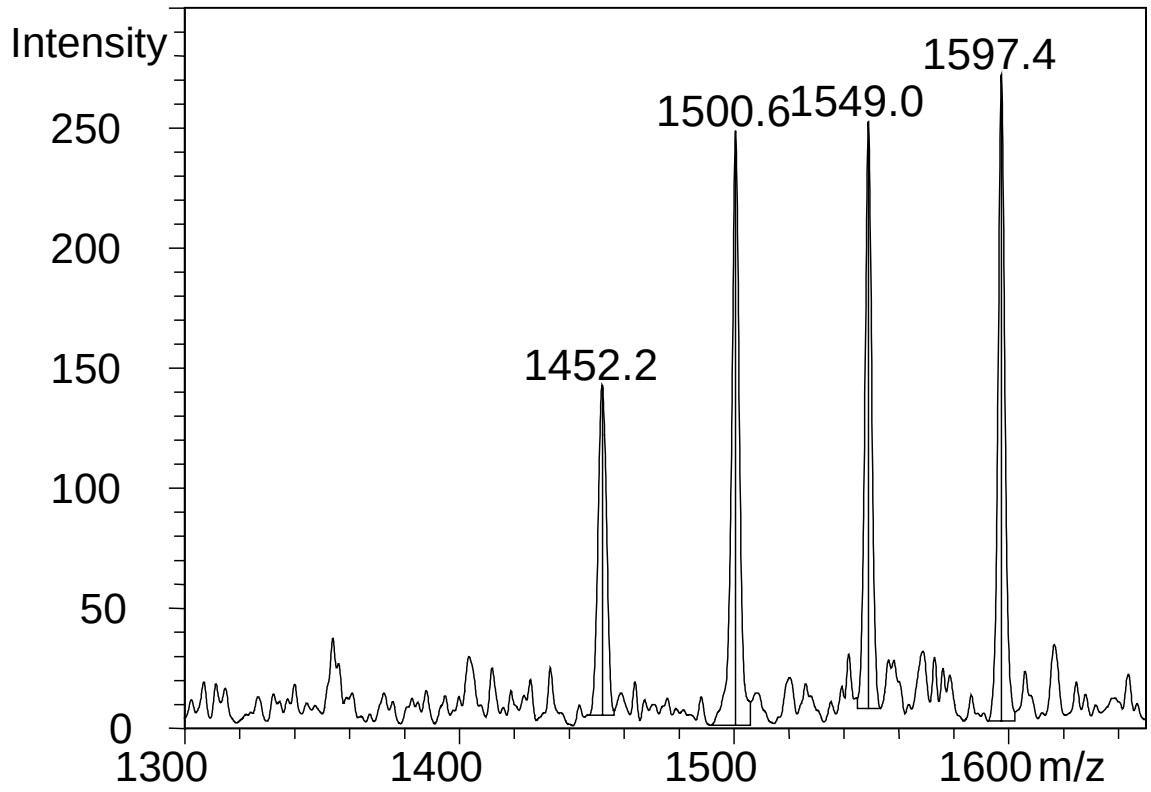

Figure S8. ESI mass spectrum of **9** (3194 Da) measured after purification**.**

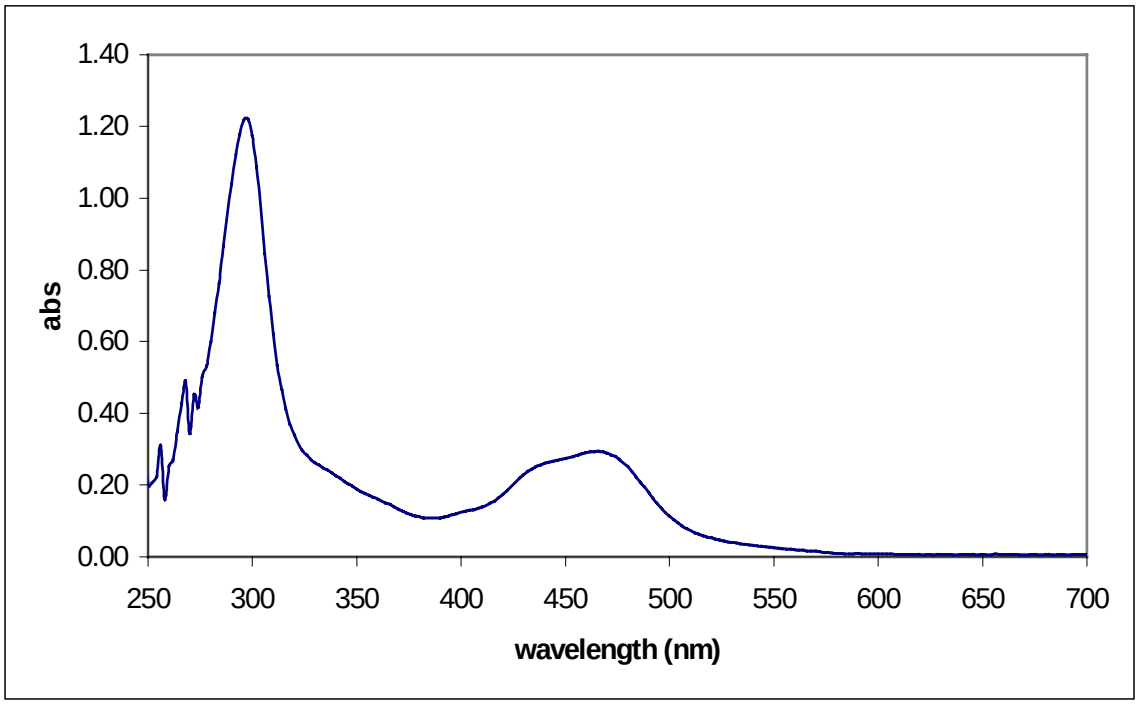

Figure S9. UV/vis absorption spectrum of **6** measured in H_2O at 298 K**.**

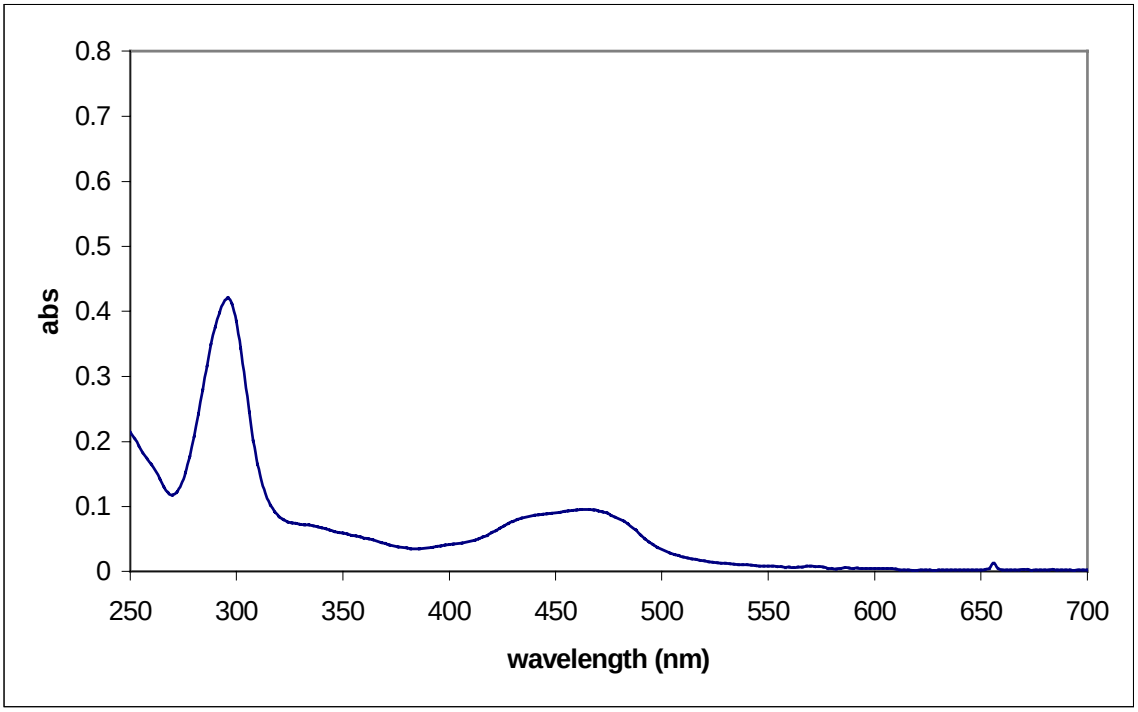

Figure S10. UV/vis absorbance spectrum of **7** in H_2O at 298 K**.**

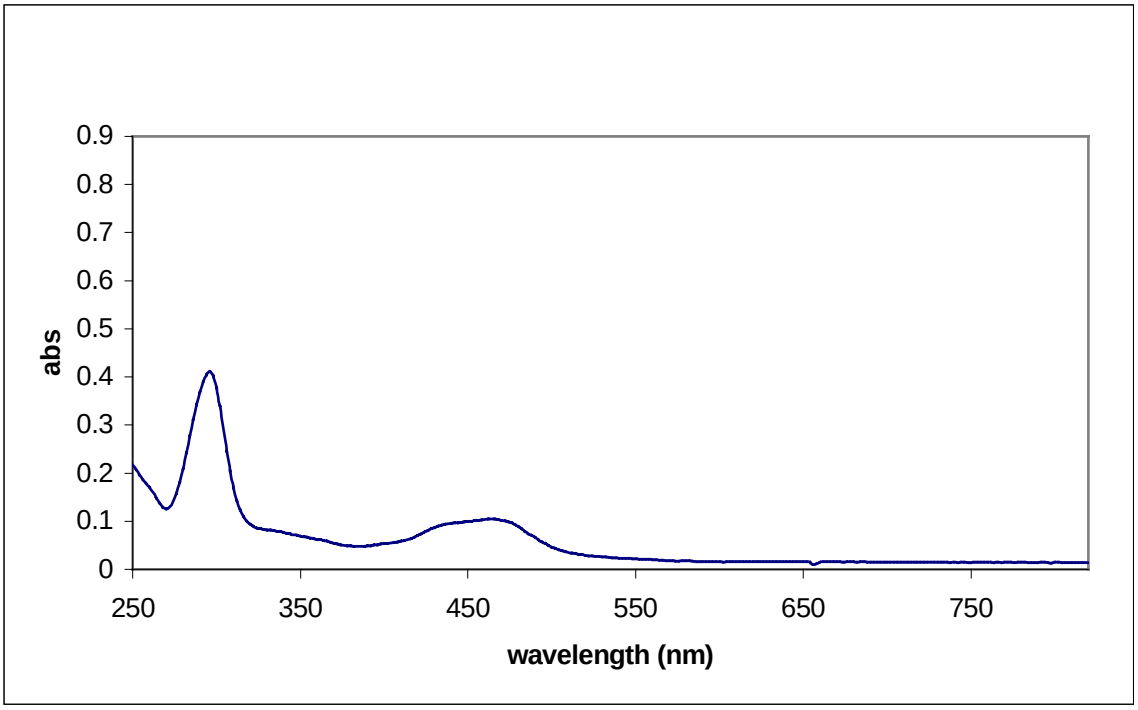

Figure S11. UV/vis absorbance spectrum of **8** in H_2O at 298 K**.**

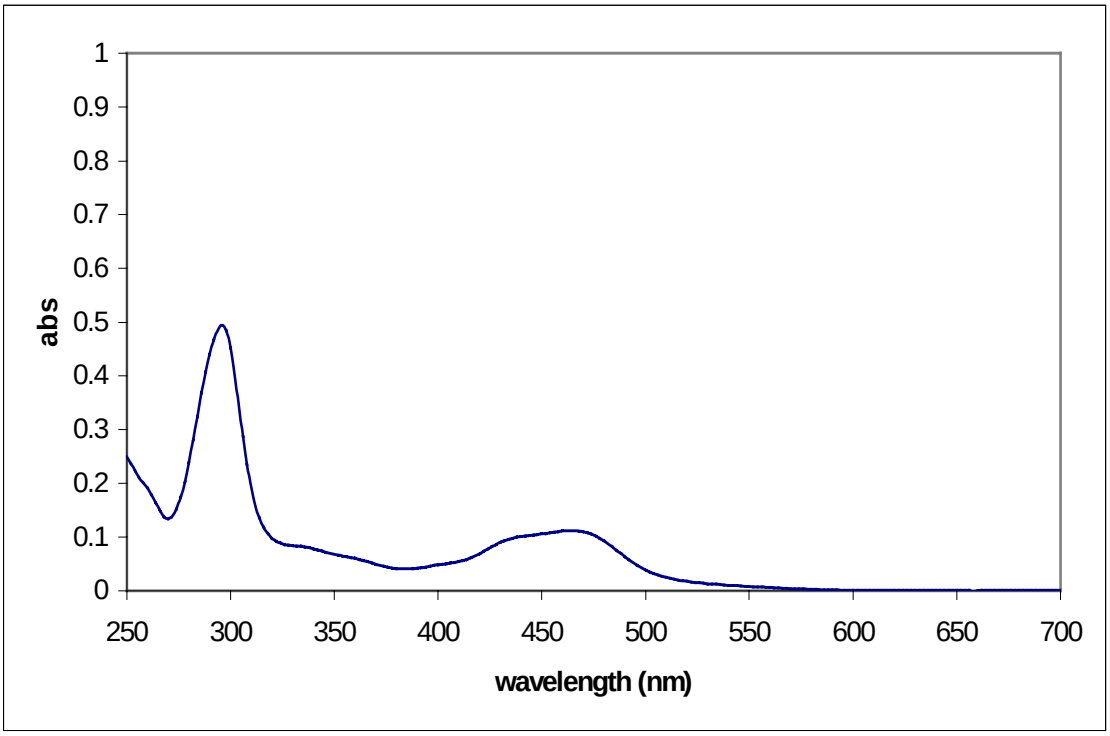

Figure S12. UV/vis absorbance spectrum of **9** in H_2O at 298 K**.**