Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Macrocyclic luminophores under confinement in a polymeric matrix - induction of large-Stokes-shift by inter-unit proton transfer

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Supporting Information

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1. General information

All solvents and chemicals used were purchased from Sigma Aldrich, TCI Europe N. V., Roth, Chem Impex Inc., and Euriso-top, were of reagent grade and were used without further purification.

^{1}H and ^{13}C NMR spectra were recorded on Bruker 400 MHz and Varian 600 MHz or 500 MHz instruments with residual solvent signal as internal standard. All 2D NMR spectra were recorded at 298 K on Varian 600 MHz with residual solvent signal as internal standard.

IR spectra were measured on JASCO FT/IR-6200.

High resolution ESI mass spectra were recorded on a SYNAPT spectrometer.

Emission spectra of polymers were measured using the FS5 spectrofluorometer from Edinburgh Instruments.

UV-Vis spectra of polymers were measured using on UV-Vis-NIR Jasco-670.

Fluorescence quantum yields of polymers were determined with the FLS 1000 spectrofluorometer from Edinburgh Instruments using integrating sphere.

2. Synthesis of luminophores

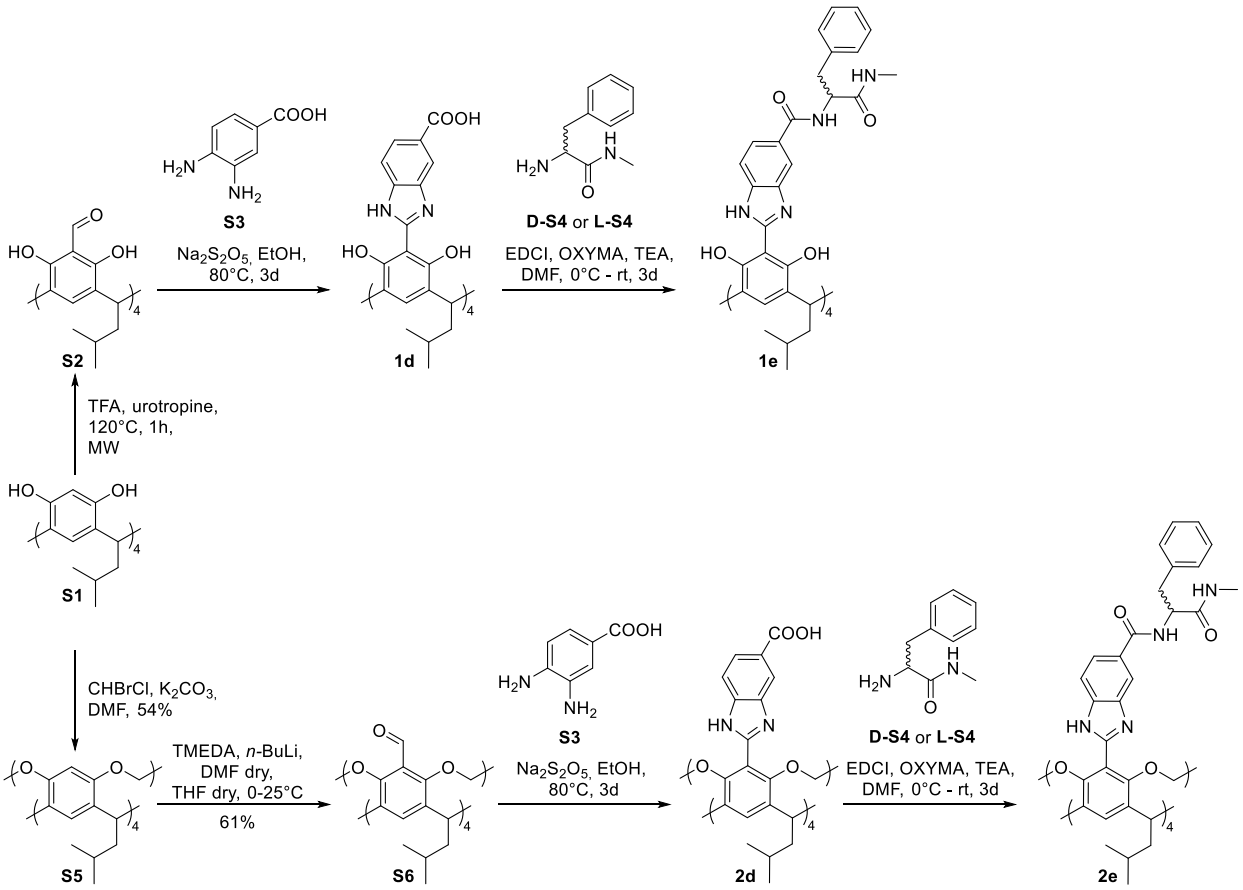


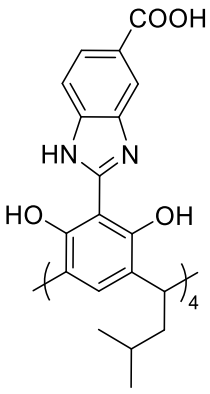
Figure S1. Synthesis of macrocyclic luminophores **1d-e** – **2d-e**.

1a: Obtained by the literature procedure.[1] Analytical data in agreement with literature data.

1b: Obtained by the literature procedure.[1] Analytical data in agreement with literature data.

1c: Obtained by the literature procedure.[1] Analytical data in agreement with literature data.

1d:



Tetraformylresorcin[4]arene **S2** (0.106 mmol) and 3,4-diaminobenzoic acid **S3** (0.426 mmol) were dissolved in ethanol (5 ml), then $Na_2S_2O_5$ solution (0.34 ml, 2.85 M) was added. The reaction mixture was stirred for 3 days at 80 °C. Then 1 M solution of HCl (2.12 ml) was added. The mixture was concentrated under reduced pressure. The precipitate was collected and washed with water and diethyl ether. Product **1d** was obtained as yellow solid, yield 98% (142 mg, 0.105 mmol).

^{1}H NMR (600 MHz, [D$_6$]DMSO, 298K) δ 8.30 (s, 4H), 7.89 (d, *J* = 8.6, 1.4 Hz, 4H), 7.86 (s, 4H), 7.75 (d, *J* = 8.5 Hz, 4H), 4.75 (t, *J* = 7.6 Hz, 4H), 2.36 (t, *J* = 6.6 Hz, 8H), 1.55 – 1.49 (m, *J* = 13.3, 6.7 Hz, 4H), 1.05 (d, *J* = 6.6 Hz, 24H).

^{13}C NMR (150 MHz, [D$_6$]DMSO, 298K) δ 167.4; 152.7; 152.3; 138.0; 134.2; 127.9; 125.5; 124.3; 116.3; 114.6; 100.5; 41.4; 31.2; 26.2; 22.7.

Diffusion coefficient (DOSY) $1.2 \cdot 10^{-10}$ m^2 s^{-1} in [D$_6$]DMSO, diameter **1.66 nm.**

HRMS (ESI): m/z calcd for $C_{76}H_{72}N_8O_{16}$+Na 1375.4964[*M* + Na]$^+$, found 1375.4991; |Δ| = 2.0 ppm.

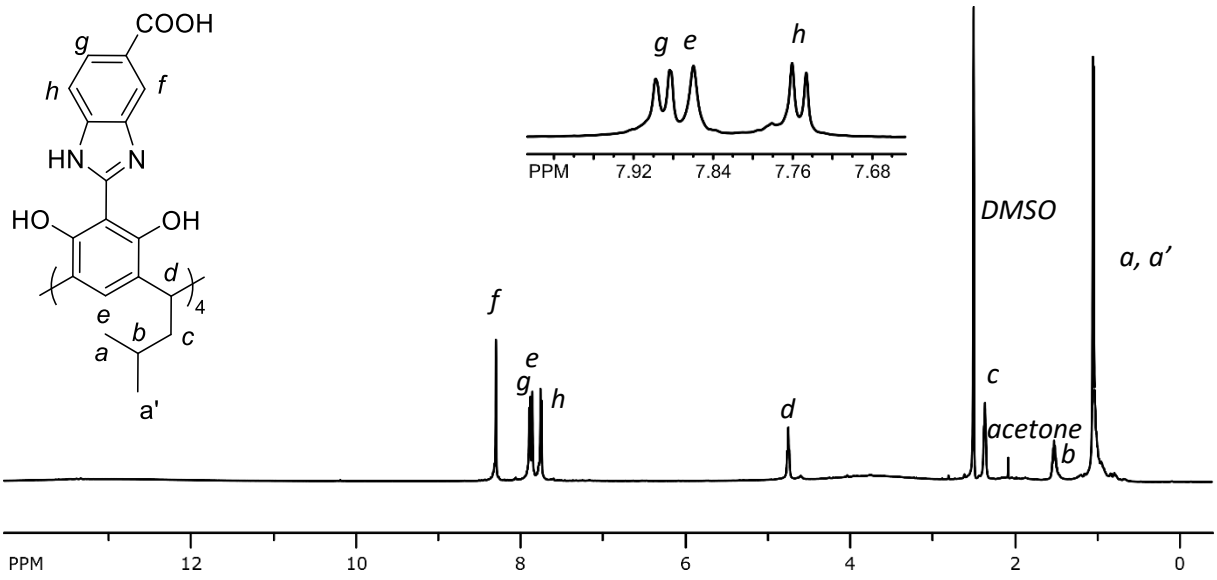


Figure S2. ^{1}H NMR spectrum of **1d** (600 MHz, [D$_6$]DMSO, 298 K).

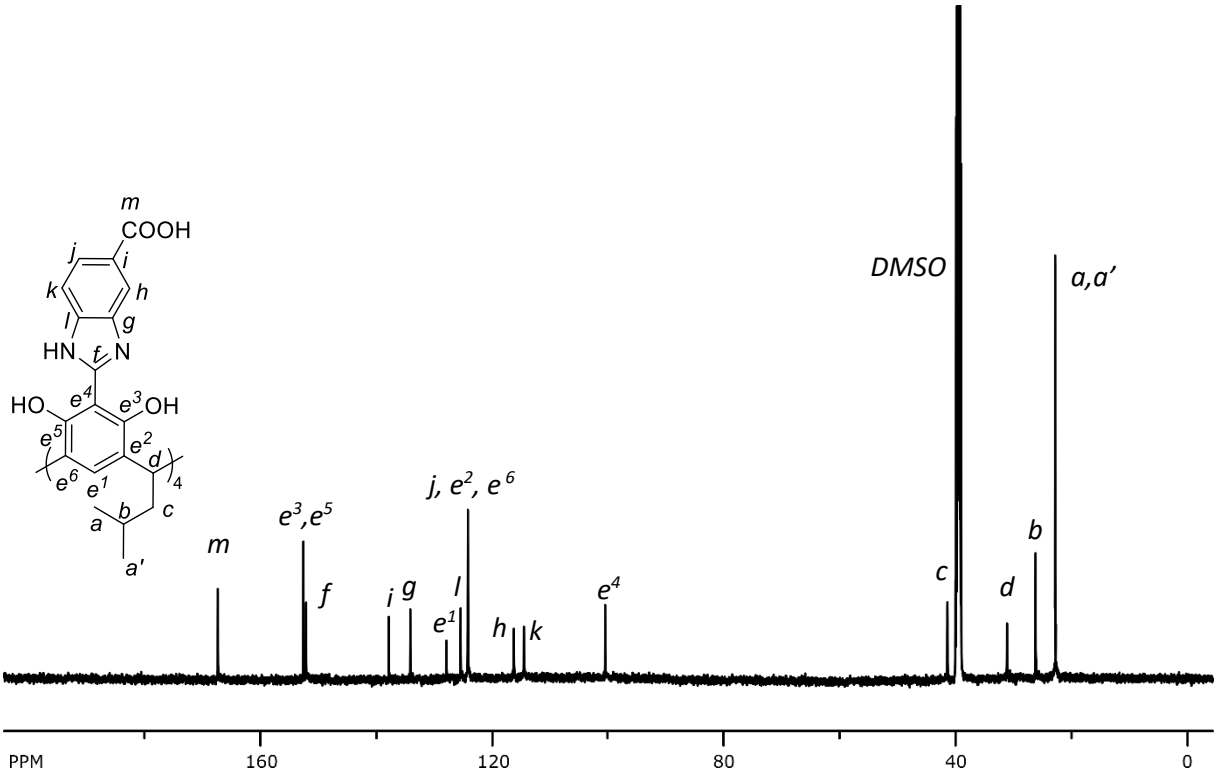


Figure S3. ^{13}C NMR spectrum of **1d** (150 MHz, [D$_6$]DMSO, 298 K).

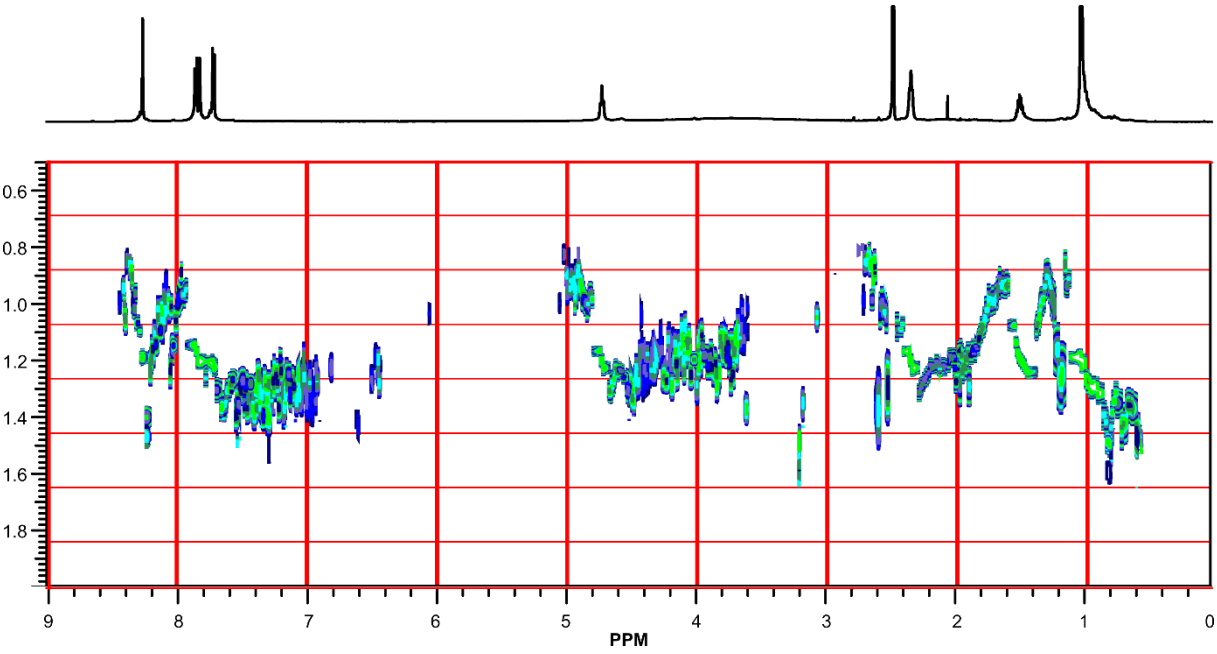


Figure S4. DOSY-NMR spectrum of **1d** (600 MHz, [D$_6$]DMSO, 298 K).

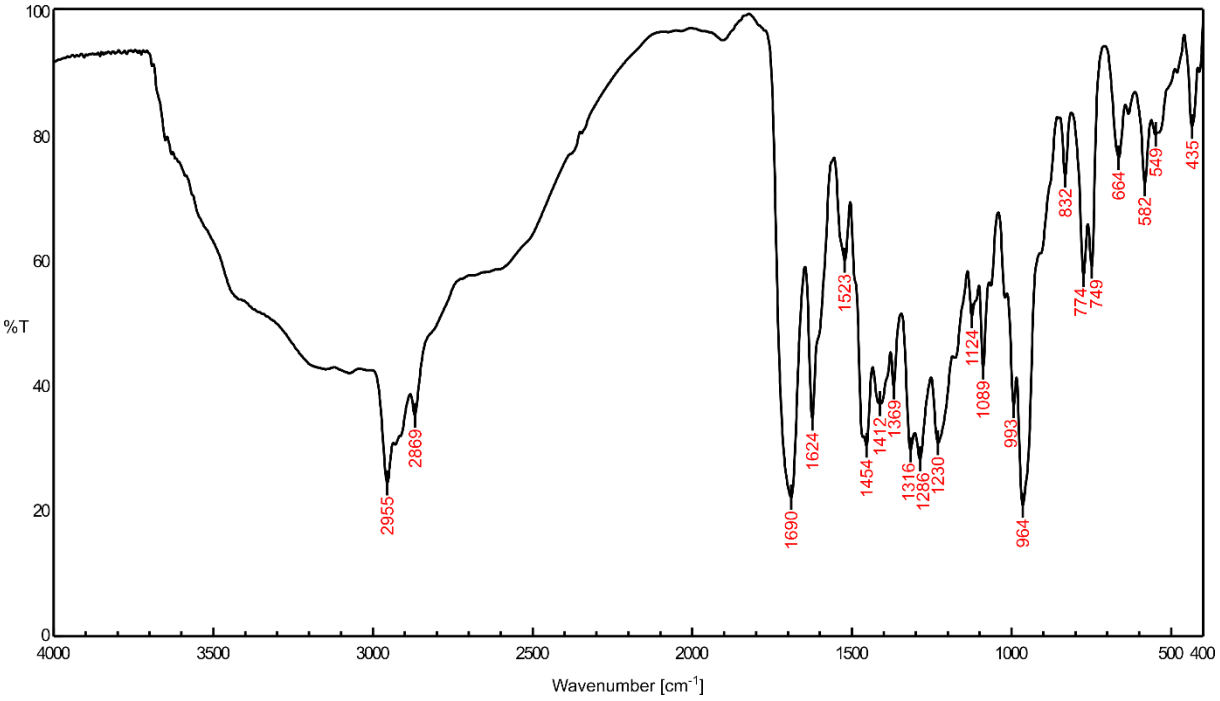
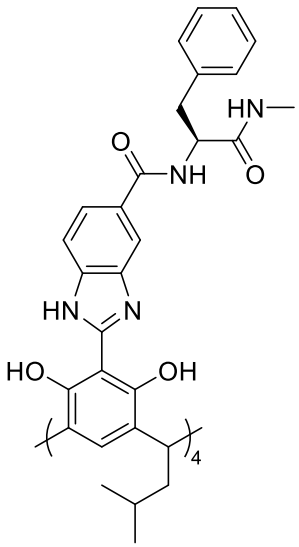


Figure S5. FT–IR (KBr) spectrum of **1d**.

D-1e:



A derivative of phenylalanine **D-S4** 4 eq. and **1d** 1 eq. were dissolved in DMF and the mixture was cooled to 0°C. Then, OXYMA (4.8 eq.) and TEA (4.8 eq.) were added. After 20 min EDC·HCl (4.8 eq.) was added. The reaction mixture was allowed to warm to rt and stirred for 3 days. Then, the reaction mixture was evaporated under reduced pressure and ethyl acetate was added and the product was precipitated. The solid was washed with water, $NaHCO_3$sat, water, citric acid (5% in H_2O) and water. The synthesis was based on general procedure. The product **D-1e** was purified by chromatography column purification 2-10% MeOH:DCM. The yellow solid was obtained, yield 42% (62 mg, 0.031 mmol).

^{1}H NMR (600 MHz, [D$_6$]DMSO, 298K) δ 8.58 (d, *J* =8.28 Hz, NH), 8.16 (s, 4H), 7.99 (q, *J* = 9.52, 4.97 Hz, NH) 7.83 (s, 4H), 7.75 (d, *J* = 8.67 Hz, 8H), 7.70 (d, *J* = 8.27 Hz, 8H), 7.33 (d, *J* = 7.78 Hz, 8H), 7.24 (t, *J* = 15.03, 7.60 Hz, 8H), 7.13 (t, *J* = 14.51, 7.60 Hz, 4H), 4.75 (t, *J* = 13.11, 6.65 Hz, 4H), 4.67 - 4.63 (m, 4H), 3.10 (dd, *J* = 13.47, 3.80 Hz, 4H), 3.00 (dd, *J* = 13.11, 11.05 Hz, 4H), 2.60 (d, *J* = 4.16 Hz, 12H), 2.36 (br t, 4H), 1.55-1.49 (m, 4H), 1.05 (d, *J* = 6.50 Hz, 24H).

^{13}C NMR (150 MHz, [D$_6$]DMSO, 298K) δ 171.7; 166.4; 152.9; 152.6; 151.9; 138.6; 136.4; 134.4; 129.2; 129.0; 128.0; 127.7; 126.1; 124.3; 124.1; 122.7; 114.5; 113.8; 100.5; 55.1; 41.3; 37.3; 31.2; 26.2; 25.6; 22.7.

Diffusion coefficient (DOSY) $1.14 \cdot 10^{-10}$ m^2 s^{-1} in [D$_6$]DMSO, diameter **1.75 nm**.

HR(ESI): m/z calcd for $C_{116}H_{118}N_{16}O_{16}$ 1990.9800[*M* - 2H]$^{2-}$; found 995.4442; |Δ| = 0.84 ppm.

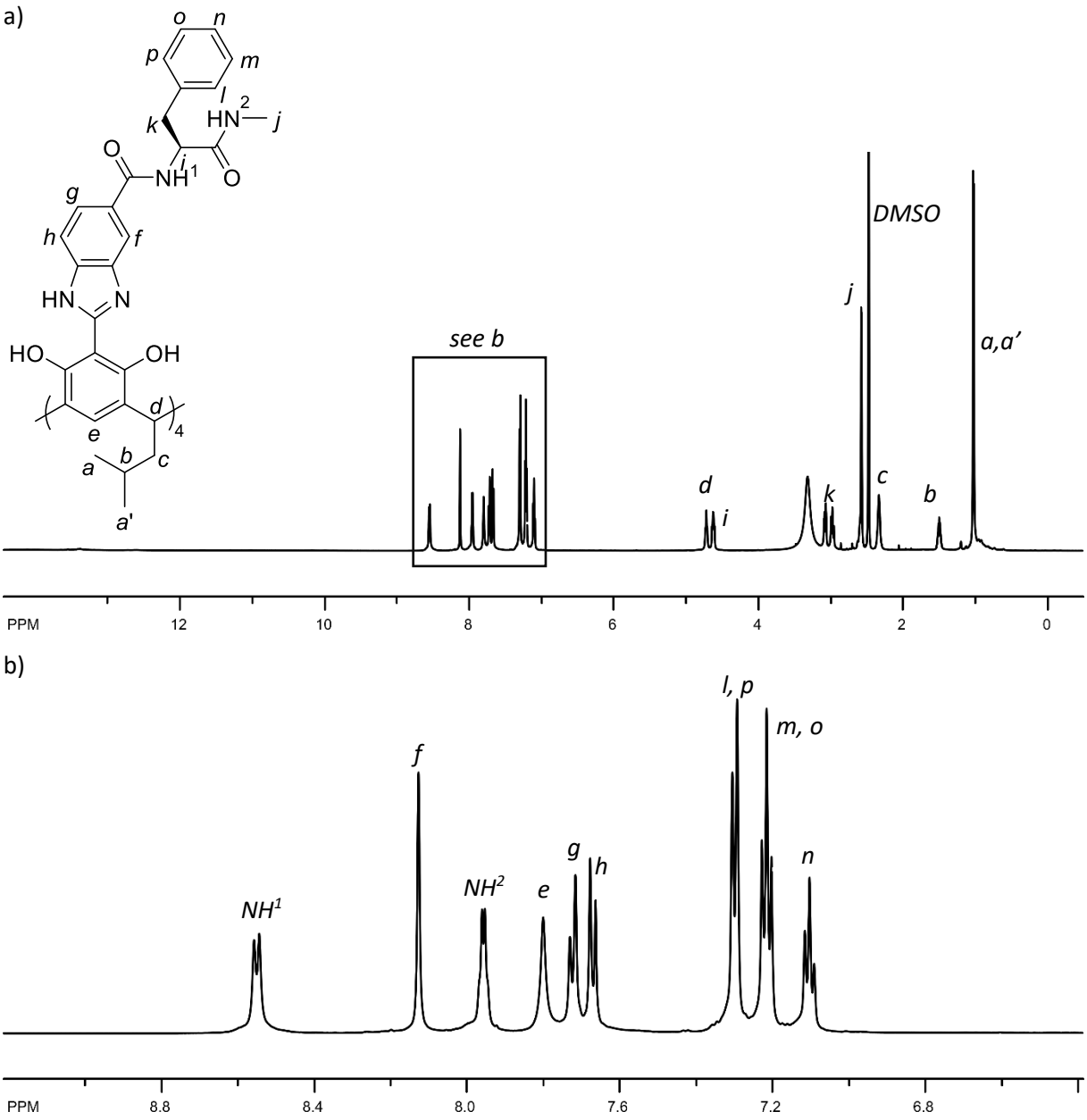


Figure S6. ^{1}H NMR spectrum of **D-1e** (600 MHz, [D_6]DMSO, 298 K).

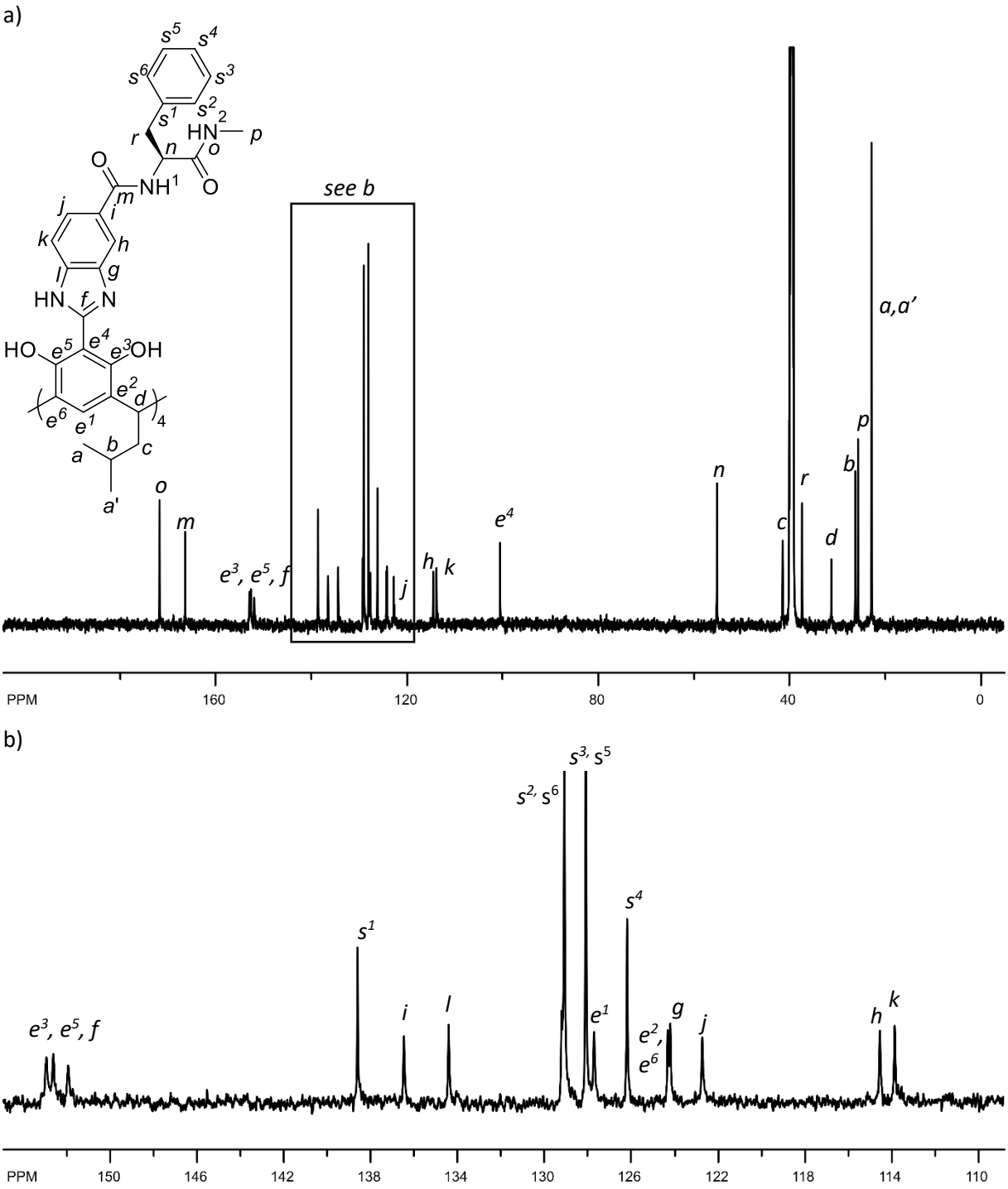


Figure S7. ^{13}C NMR spectrum of **D-1d** (150 MHz, [D_6]DMSO, 298 K).

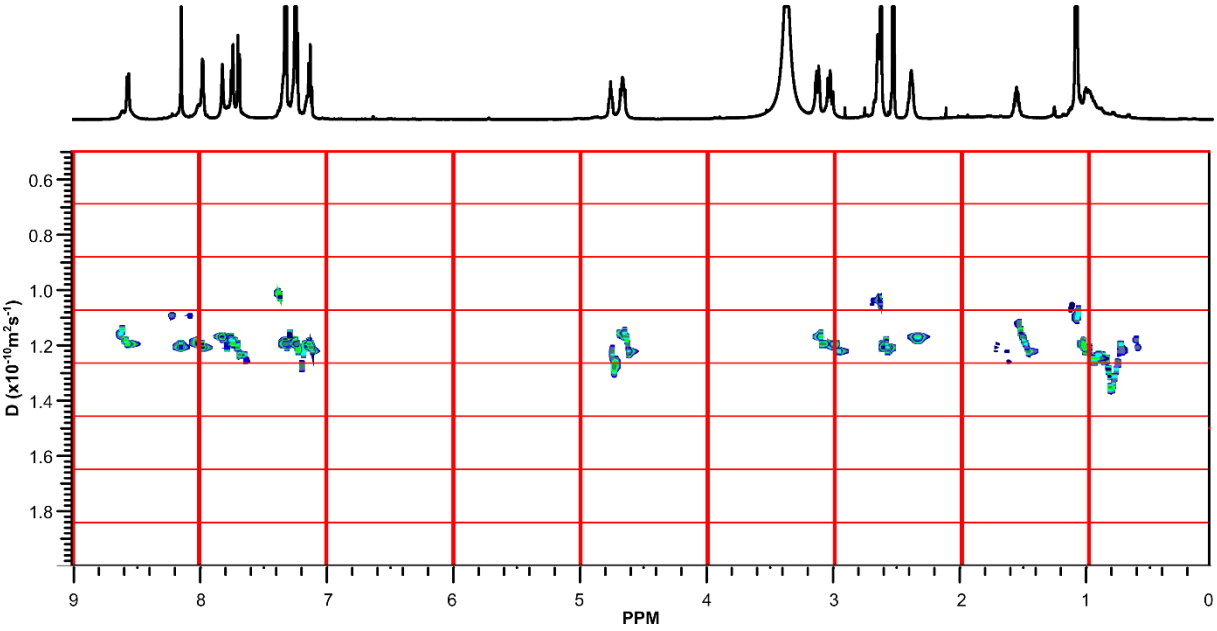


Figure S8. DOSY-NMR spectrum of **D-1e** (600 MHz, [D_6]DMSO, 298 K).

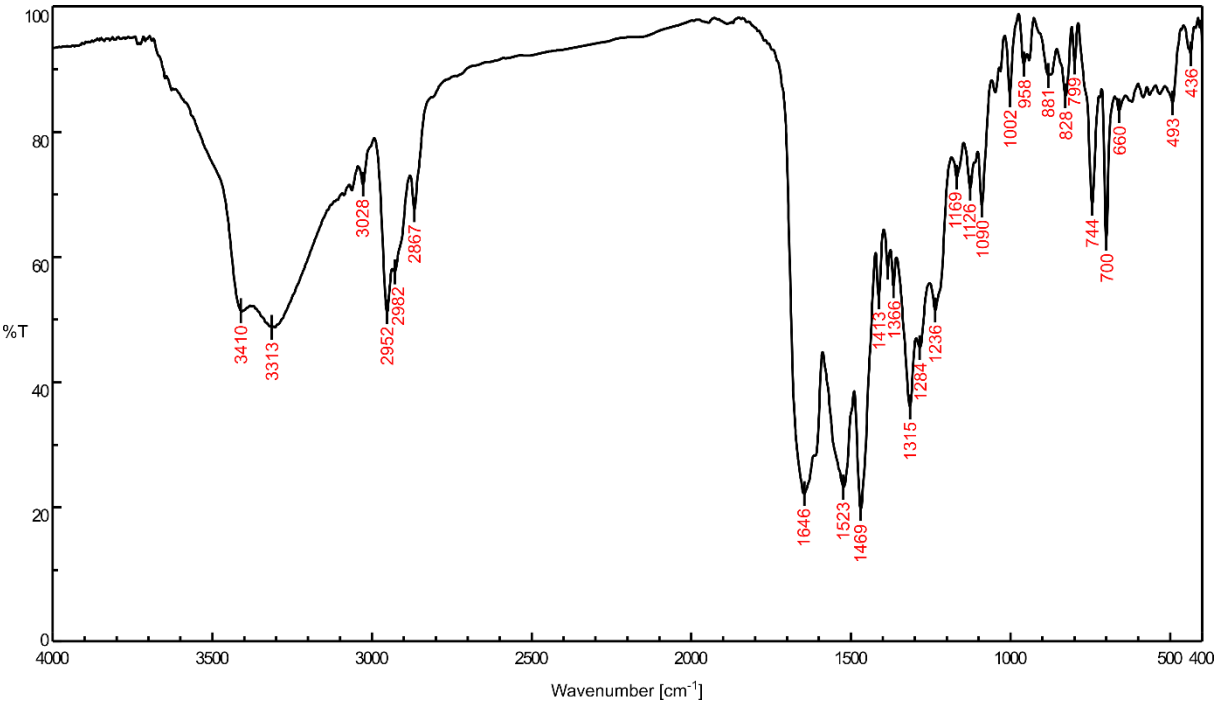


Figure S9. FT–IR (KBr) spectrum of **D-1e**.

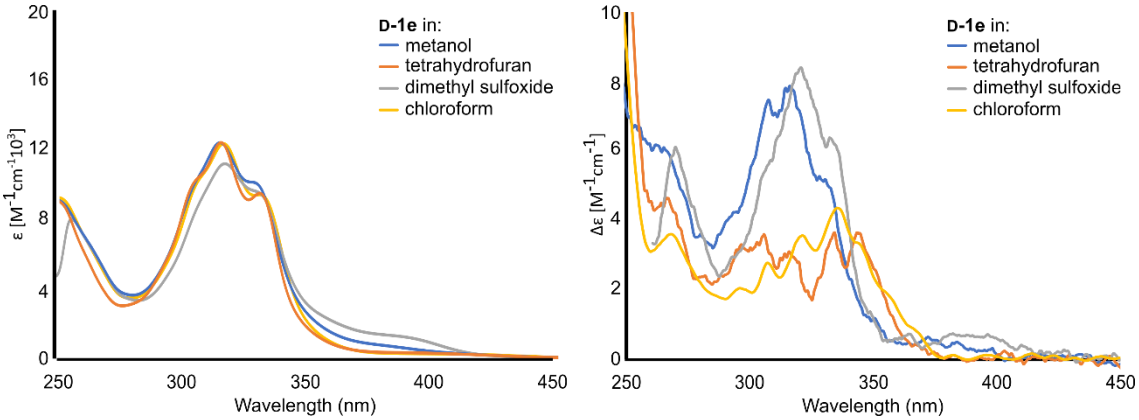
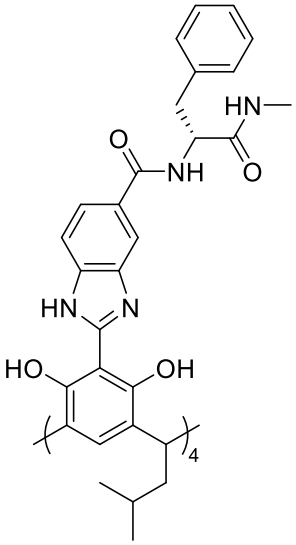


Figure S10. UV and ECD spectra in different solvents of **D-1e**.

L-1e:



A derivative of phenylalanine **L-S4** 4 eq. and **1d** 1 eq. were dissolved in DMF and the mixture was cooled to 0°C. Then, OXYMA (4.8 eq.) and TEA (4.8 eq.) were added. After 20 min EDC·HCl (4.8 eq.) was added. The reaction mixture was allowed to warm to rt and stirred for 3 days. Then, the reaction mixture was evaporated under reduced pressure and ethyl acetate was added and the product was precipitated. The solid was washed with water, $NaHCO_3$sat, water, citric acid (5% in H_2O) and water. The synthesis was based on general procedure. The product **L-1e** was purified by chromatography column purification 2-10% MeOH:DCM. The white solid was obtained, yield 46% (68 mg, 0.034 mmol).

Analytical data in agreement with data for **D-1e**.

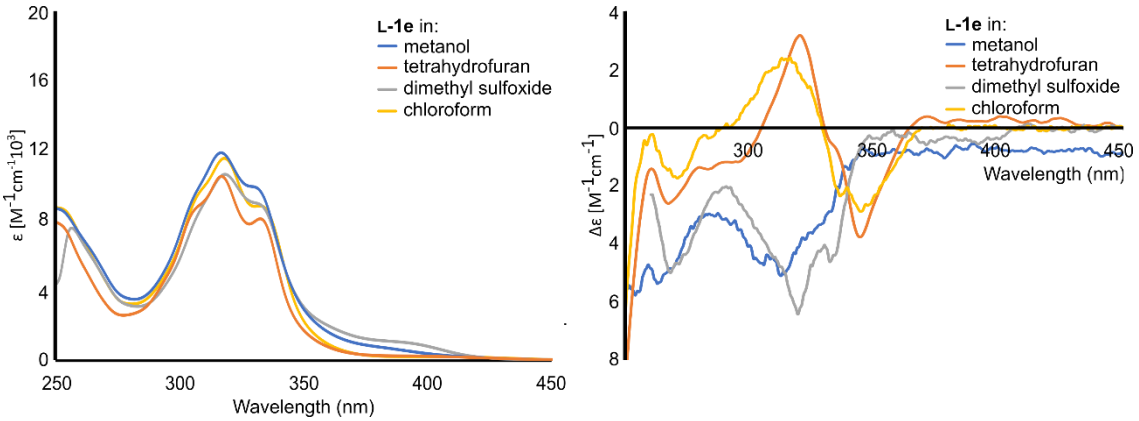


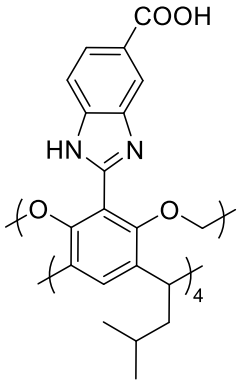
Figure S11. UV and ECD spectra in different solvents of **L-1e**.

2a: Obtained by the literature procedure.[1] Analytical data in agreement with literature data.

2b: Obtained by the literature procedure.[1] Analytical data in agreement with literature data.

2c: Obtained by the literature procedure.[1] Analytical data in agreement with literature data.

2d:



Tetraformylresorcin[4]arene **S6** (0.106 mmol) and 3,4-diaminobenzoic acid **S3** (0.426 mmol) were dissolved in ethanol (5 ml), then $Na_2S_2O_5$ solution (0.34 ml, 2.85 M) was added. The reaction mixture was stirred for 3 days at 80 °C. Then 1 M solution of HCl (2.12 ml) was added. The precipitate was collected and washed with water and diethyl ether. Product **2d** was obtained as white solid, yield 82% (46 mg, 0.0328 mmol).

^{1}H NMR (600 MHz, [D$_6$]DMSO, 298 K) δ 8.12 (s, 4H), 7.99 (s, 4H), 7.79 (d, *J* = 8.50 Hz, 4H), 7.59 (d, *J* = 7.72 Hz, 4H), 5.34 (d, *J* = 7.61 Hz, 4H), 4.97 (d, *J* = 7.67 Hz, 4H), 4.56 (d, *J* = 7.35 Hz, 4H), 2.46 (overlay with DMSO, 8H), 1.65- 1.58 (m, 4H), 1.08 (d, *J* = 6.25 Hz, 24H).

^{13}C NMR (150 MHz, [D$_6$]DMSO, 298 K) δ 187.2; 168.2; 153.1; 148.1; 139.1; 124.8; 124.6;123.7; 120.5; 100.2; 99.9; 38.5; 35.0; 26.6; 23.1.

Diffusion coefficient (DOSY) $1.5 \cdot 10^{-10}$ m^2 s^{-1} in [D$_6$]DMSO, **diameter 1.33 nm**.

HRMS (ESI): m/z calcd for $C_{80}H_{72}N_8O_{16}$+H: 1401.5145[*M* + H]$^+$; found 1401.5161; |Δ| = 1.1 ppm.

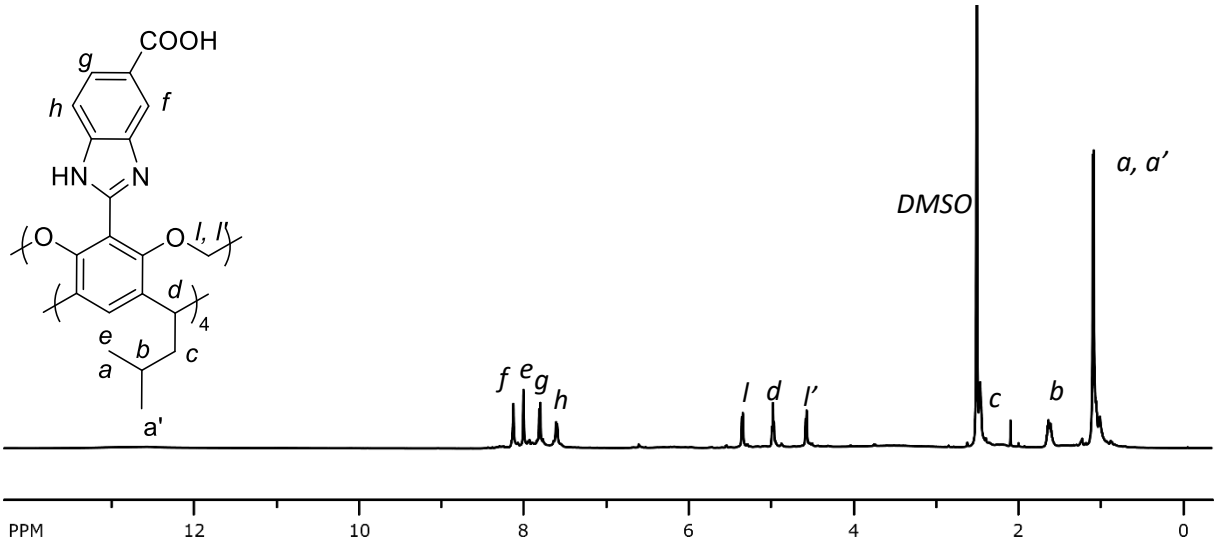


Figure S12. ^{1}H NMR spectrum of **2d** (600 MHz, [D$_6$]DMSO, 298 K).

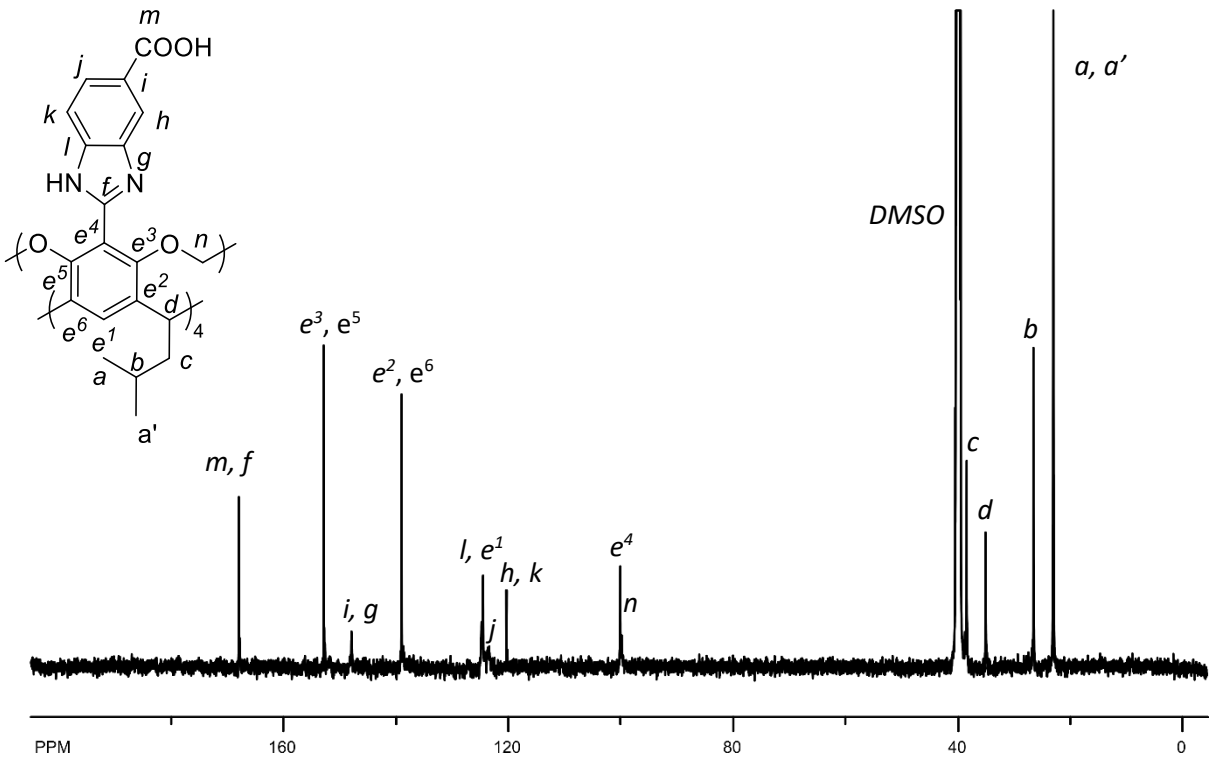


Figure S13. ^{13}C NMR spectrum of **2d** (150 MHz, [D_6]DMSO, 298 K).

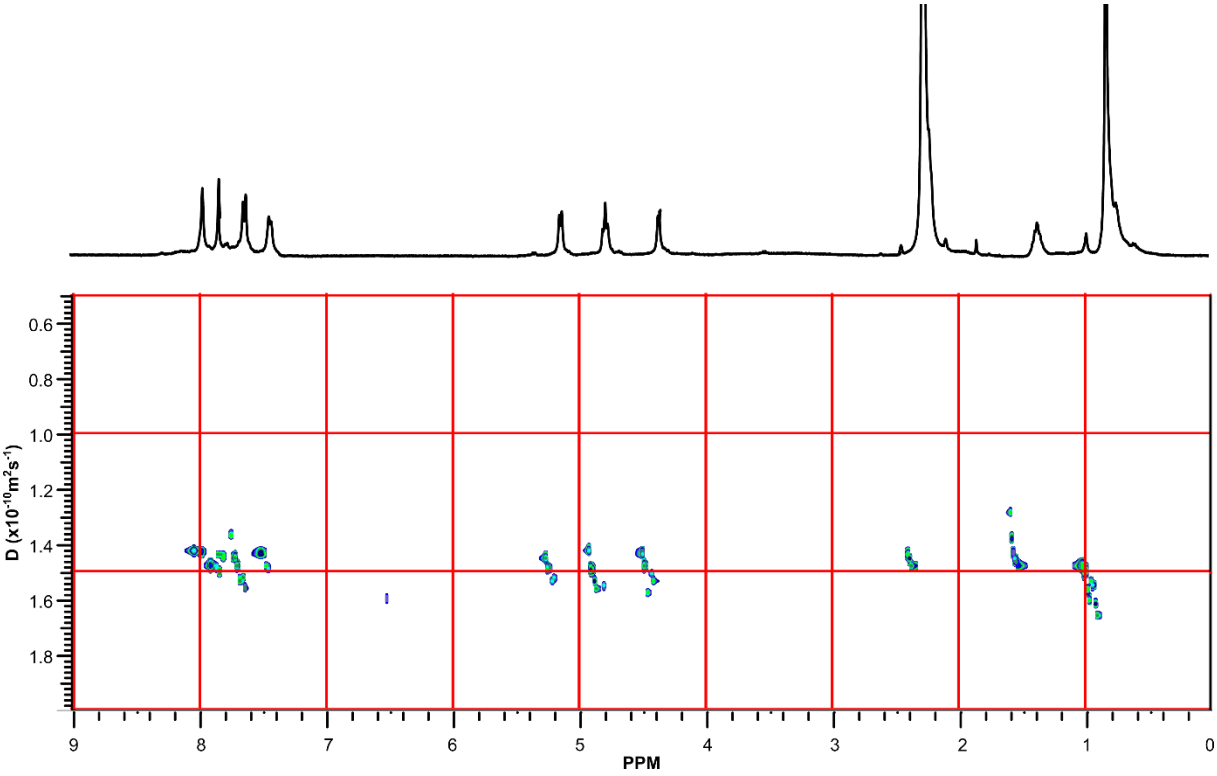


Figure S14. DOSY-NMR spectrum of **2d** (600 MHz, [D_6]DMSO, 298 K).

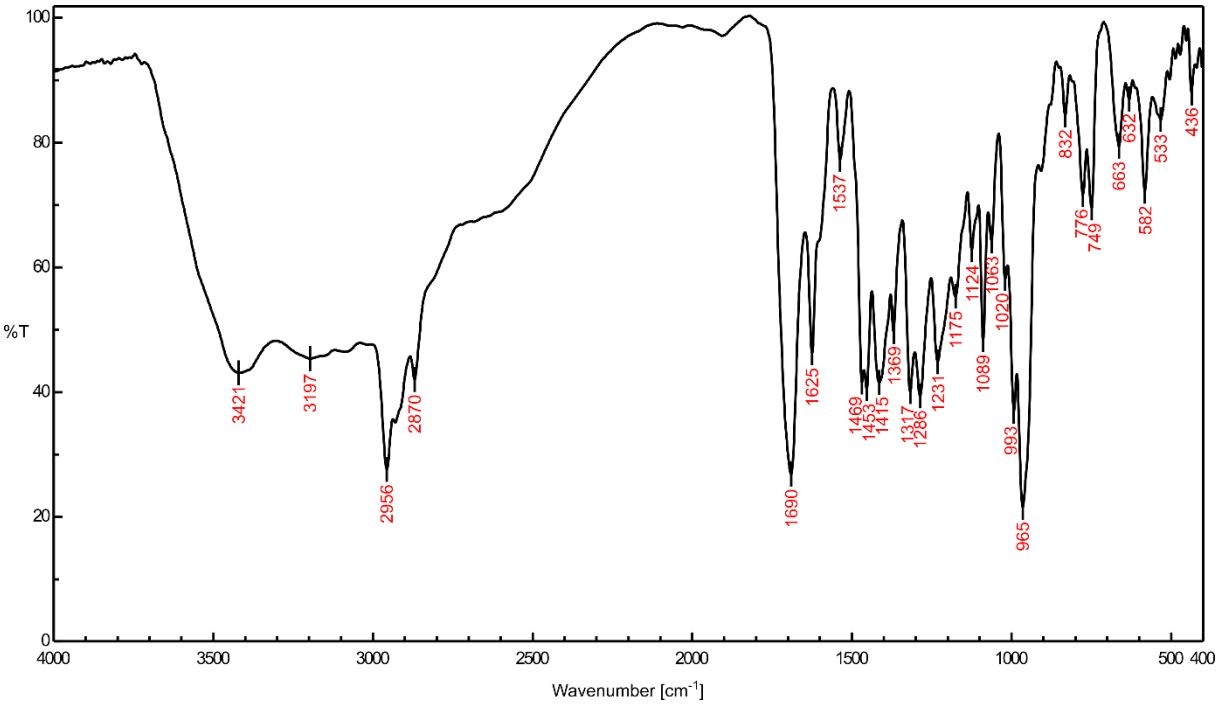
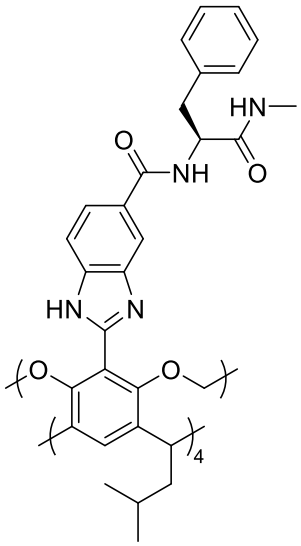


Figure S15. FT–IR (KBr) spectrum of **2d**.

D-2e:



A derivative of phenylalanine **D-S4** 4 eq. and **2d** 1 eq. were dissolved in DMF and the mixture was cooled to 0°C. Then, OXYMA (4.8 eq.) and TEA (4.8 eq.) were added. After 20 min EDC·HCl (4.8 eq.) was added. The reaction mixture was allowed to warm to rt and stirred for 3 days. Then, the reaction mixture was evaporated under reduced pressure and ethyl acetate was added and the product was precipitated. The solid was washed with water, $NaHCO_3$sat, water, citric acid (5% in H_2O) and water. The synthesis was based on general procedure. The product **D-2e** was obtained as white solid, yield 64 % (47 mg, 0.023 mmol).

^{1}H NMR (600 MHz, [D$_6$]DMSO, 298K) δ (broad spectrum) 12.65 (NH), 8.54 (s, NH), 8.17 (s, 4H), 7.97 (s, 4H), 7.95 (br s, 2H), 7.91 (br s, 2H), 7.66 (br q, NH), 7.60 (m, 2H) 7.44 (m, 2H), 7.29 (br d, 8H), 7.20 (br t, 8H), 7.09 (br t, 4H), 5.33-5.26 (m, 4H), 4.98 (br t, 4H), 4.66 (br t, 4H), 4.54 (br d, *J* = 18.74 Hz, 4H), 3.08 (br dd, 4H), 2.99 (br dd, 4H), 2.59 (br d, 12H), 2.45 (br t, 4H), 1.64-1.59 (m, 4H), 1.08 (br d, 24H).

^{13}C NMR (150 MHz, [D$_6$]DMSO, 298K) δ 171.8; 166.3; 152.6; 147.6; 146.8; 145.2; 142.5; 138.6; 136.2; 133.4; 129.0; 128.2; 127.9; 126.0; 124.0; 122.4; 120.1; 118.4; 118.2; 111.2, 110.9; 99.6; 54.9; 38.0; 37.2; 34.6; 26.1; 25.6; 22.6.

Diffusion coefficient (DOSY) $1.34 \cdot 10^{-10}$ m^2 s^{-1} in [D$_6$]DMSO, diameter **1.49 nm**.

HR MS (ESI): m/z calcd for $C_{120}H_{122}N_{16}O_{16}$ 2042.9214[*M* - 2H]$^{2-}$, found 1021.4622; |Δ|= 1.48 ppm.

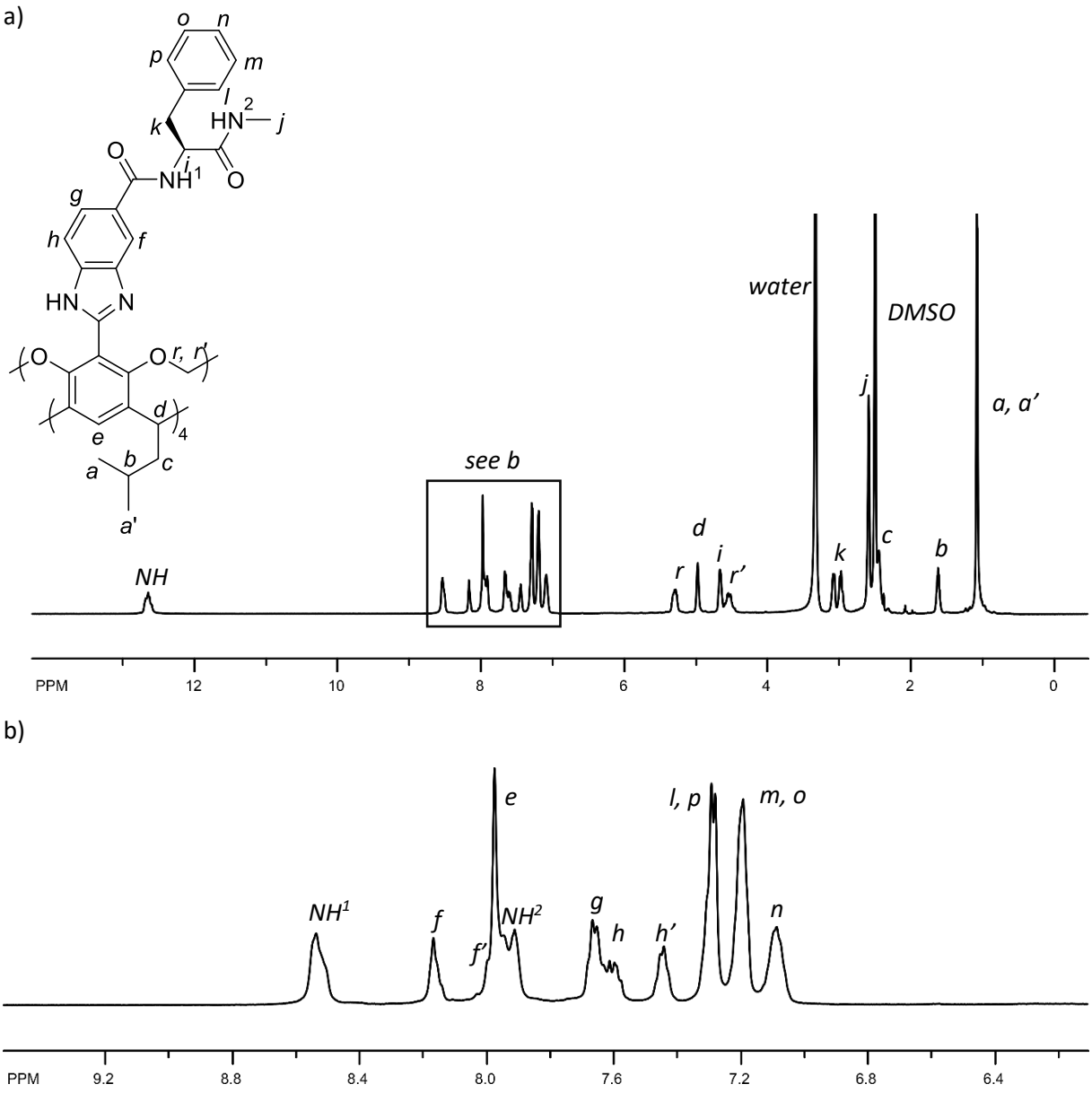


Figure S16. ^{1}H NMR spectrum of **D-2e** (600 MHz, [D_6]DMSO, 298 K).

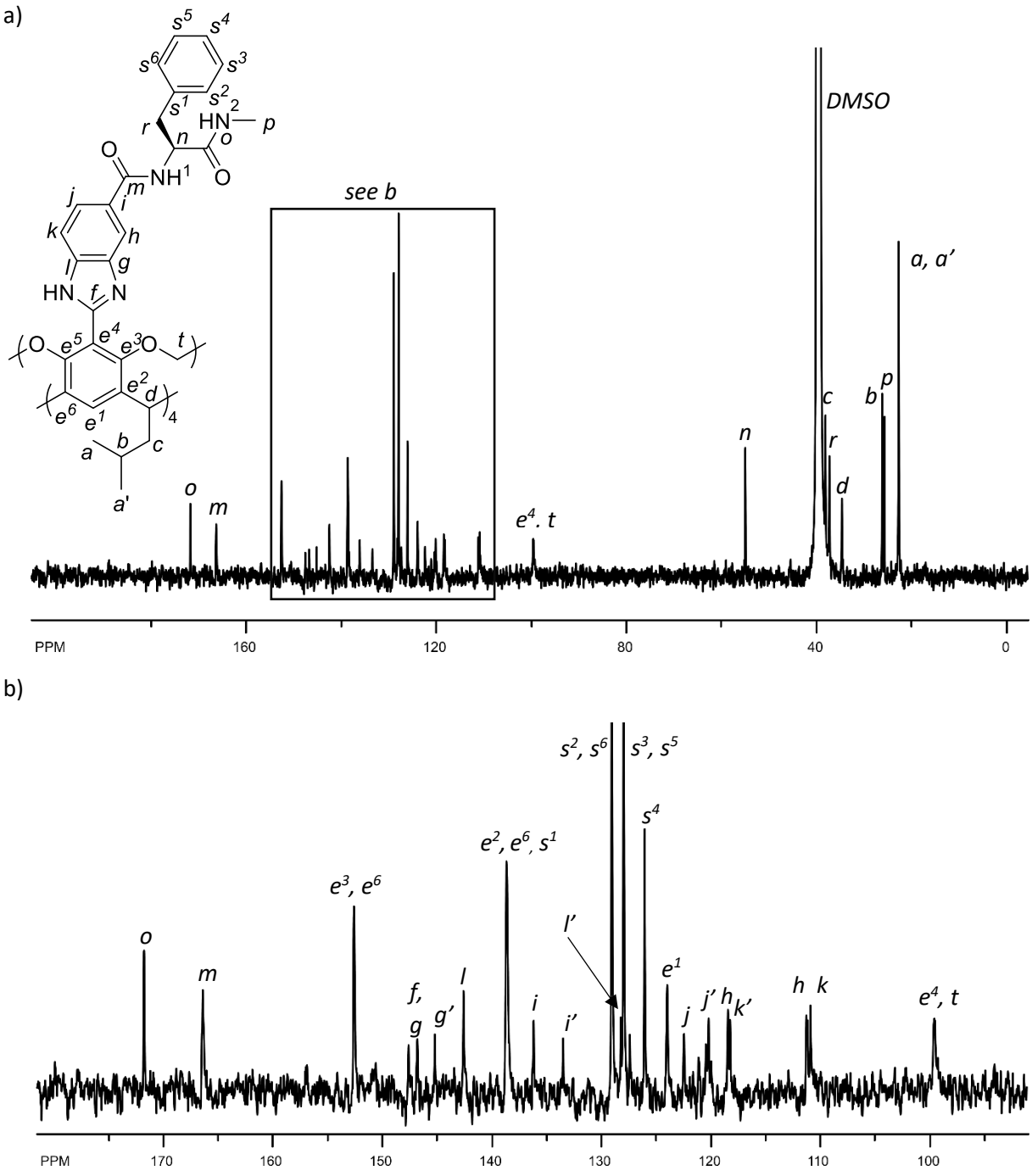


Figure S17. ^{13}C NMR spectrum of **D-2e** (150 MHz, [D_6]DMSO, 298 K).

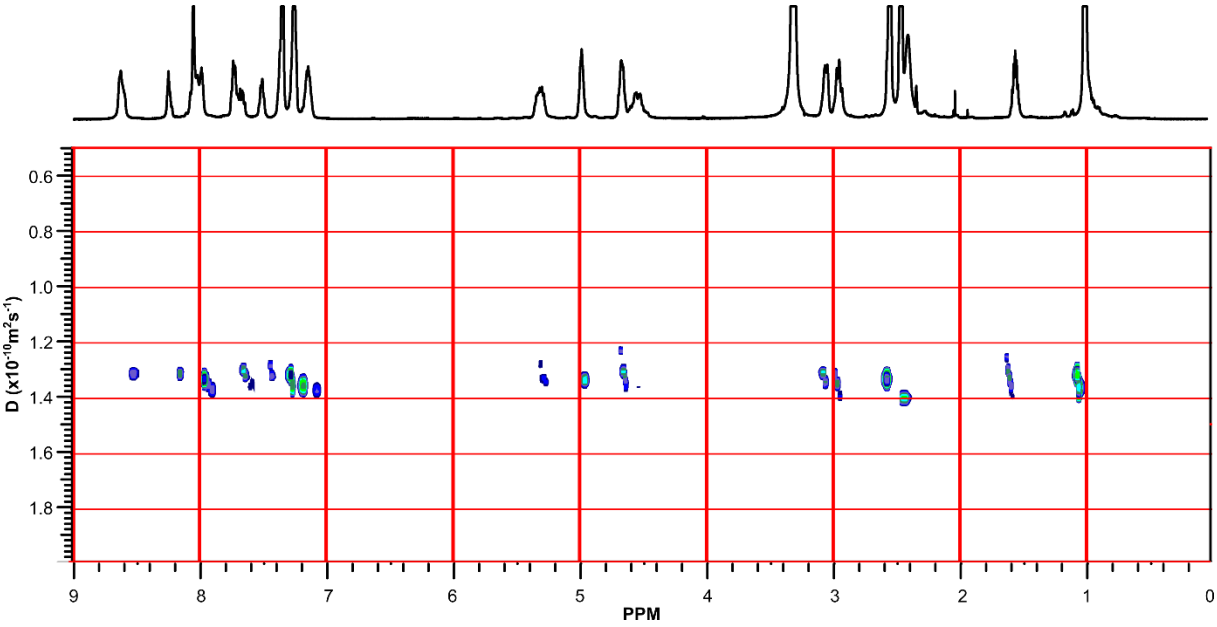


Figure S18. DOSY-NMR spectrum of **D-2e** (600 MHz, [D_6]DMSO, 298 K).

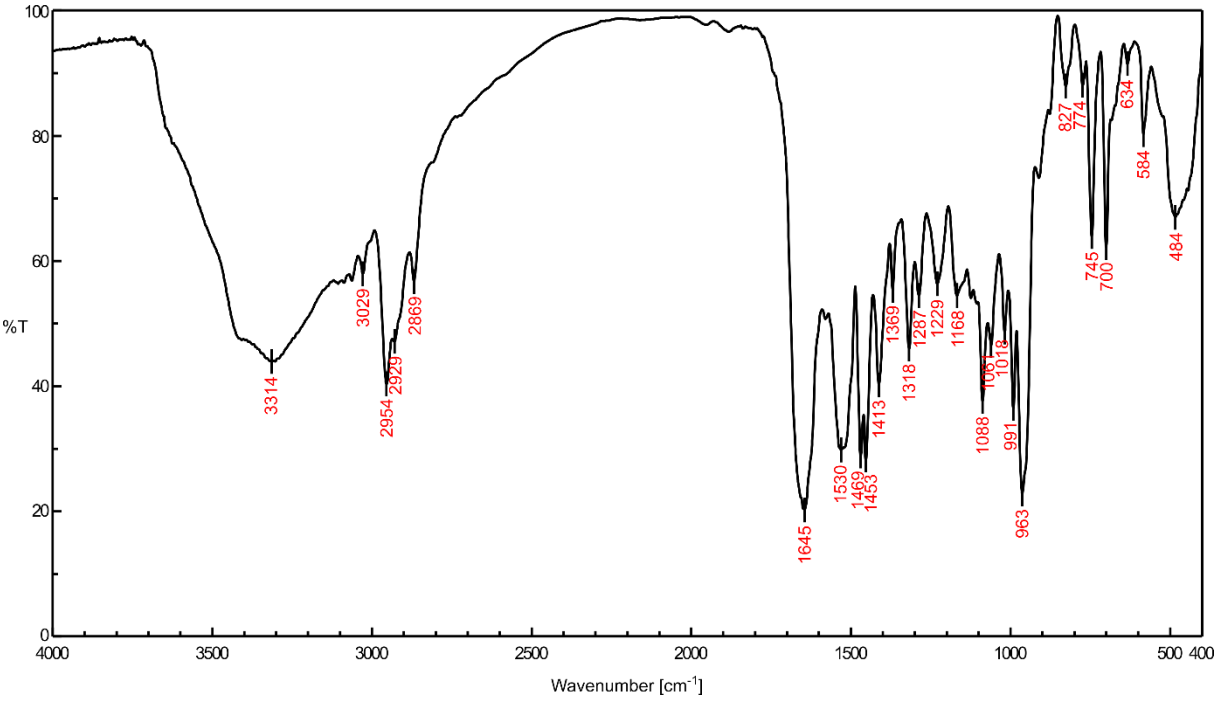


Figure S19. FT–IR (KBr) spectrum of **D-2e**.

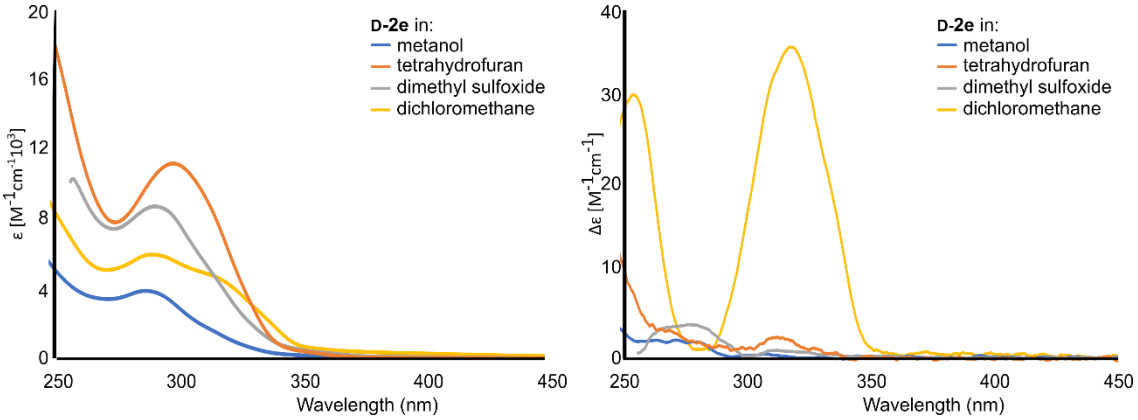
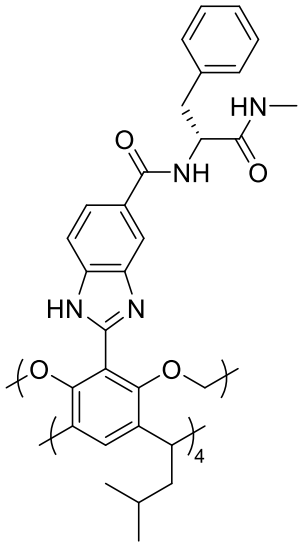


Figure S20. UV and ECD spectra in different solvents of **D-2e**.

L-2e:



A derivative of phenylalanine **L-S4** 4 eq. and **2d** 1 eq. were dissolved in DMF and the mixture was cooled to 0 °C. Then, OXYMA (4.8 eq.) and TEA (4.8 eq.) were added. After 20 min EDC·HCl (4.8 eq.) was added. The reaction mixture was allowed to warm to rt and stirred for 3 days. Then, the reaction mixture was evaporated under reduced pressure and ethyl acetate was added and the product was precipitated. The solid was washed with water, $NaHCO_3$sat, water, citric acid (5% in H_2O) and water. The product **L-2e** was obtained as white solid, yield 27% (20 mg, 0.0098 mmol).

Analytical data in agreement with data for **D-2e**.

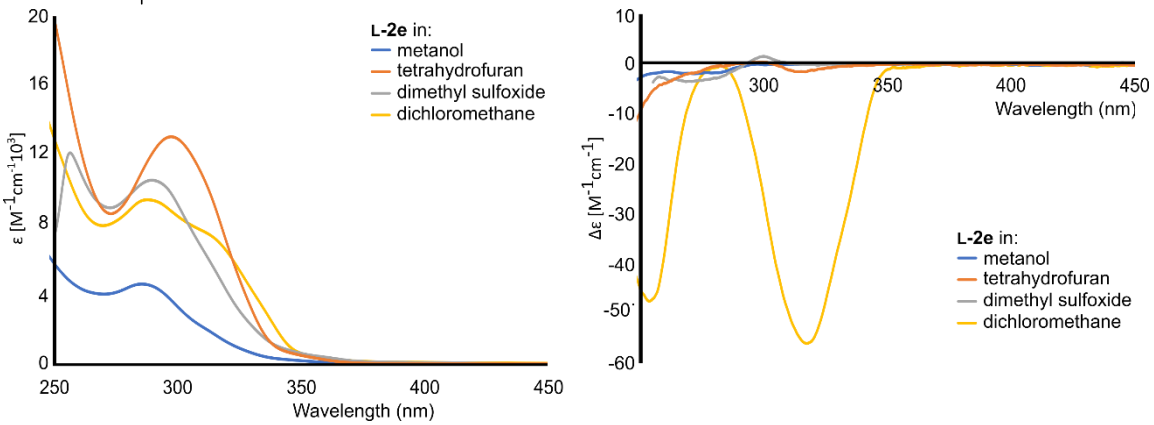


Figure S21. UV and ECD spectra in different solvents of **L-2e**.

3a: Obtained by the literature procedure.[1] Analytical data in agreement with literature data.

3b: Obtained by the literature procedure.[1] Analytical data in agreement with literature data.

3c: Obtained by the literature procedure.[1] Analytical data in agreement with literature data.

4a: Obtained by the literature procedure.[1] Analytical data in agreement with literature data.

4b: Obtained by the literature procedure.[1] Analytical data in agreement with literature data.

4c: Obtained by the literature procedure.[1] Analytical data in agreement with literature data.

3. Preparation of PMMA-1a÷4c

Method A: To a mixture of methyl methacrylate (MMA, 2ml) and benzoyl peroxide (10 mg) in a 4 ml sealed vial a luminophore (**1a÷4c**, 0.4 mg) was added. The mixture was sonicated for 30 s and then heated at 80 °C for 30 minutes, then at 40 °C for 16 h and, finally, at 90 °C for 4 h. After that period the samples were opened and kept at 60 °C for 2 days to dry. The vials were removed by breaking the glass and the samples were analyzed.

Method B: To a mixture of methyl methacrylate (MMA, 4 ml) and benzoyl peroxide (20 mg) in a 4 ml sealed vial a luminophore (**1a÷4c**, 0.8 mg) was added. The mixture was sonicated for 30 s and then heated at 80 °C for 1 hour. When the mixture became a gel, it was poured onto a flat glass vial. After evaporation of the residual methyl methacrylate, the fluorescent polymer was obtained in the form of a thin plate.

3.1 UV-Vis and FL spectra

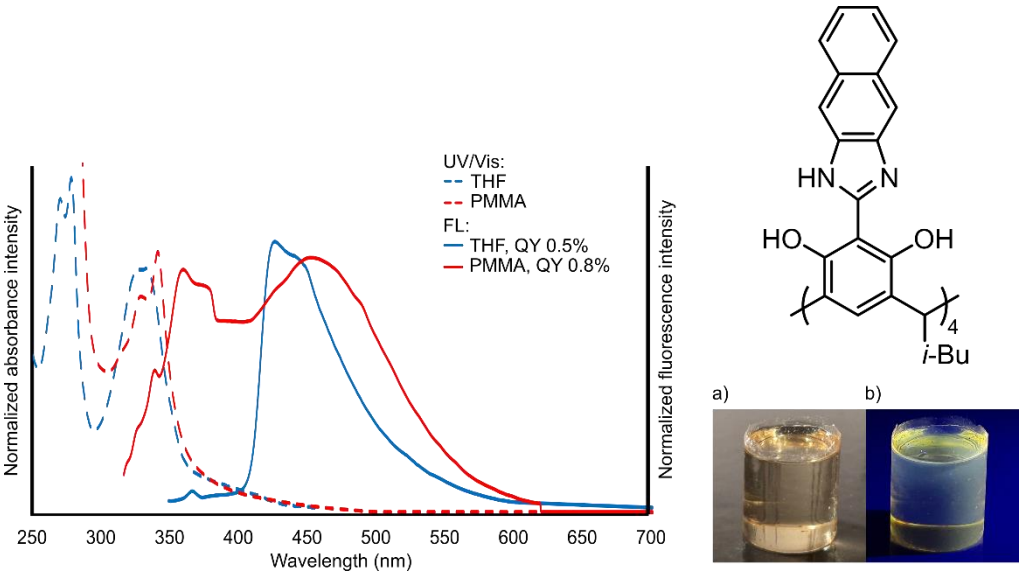


Figure S22. FL and UV properties of **1a**: FL and UV spectra in solution (blue line, C = $4.0 \cdot 10^{-6}$ M, λ_{ex} = 350 nm), FL and UV spectra in PMMA (red line, C = 0.2%, λ_{ex} = 320 nm); a) **PMMA-1a** under ambient light; b) **PMMA-1a** under UV light.

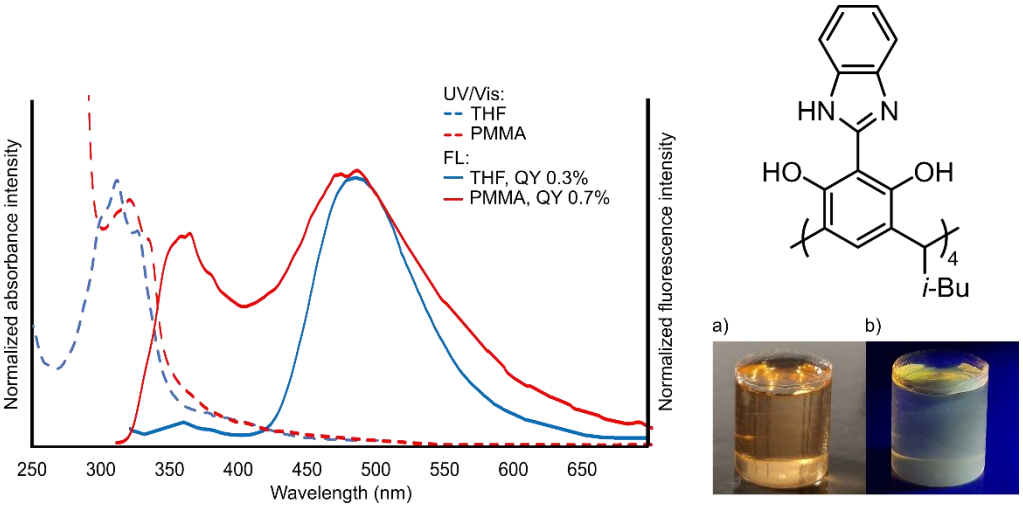


Figure S23. FL and UV properties of **1b**: FL and UV spectra in solution (blue line, C = $4.0 \cdot 10^{-6}$ M, λ_{ex} = 310 nm), FL and UV spectra in PMMA (red line, C = 0.2%, λ_{ex} = 310 nm); a) **PMMA-1b** under ambient light; b) **PMMA-1b** under UV light.

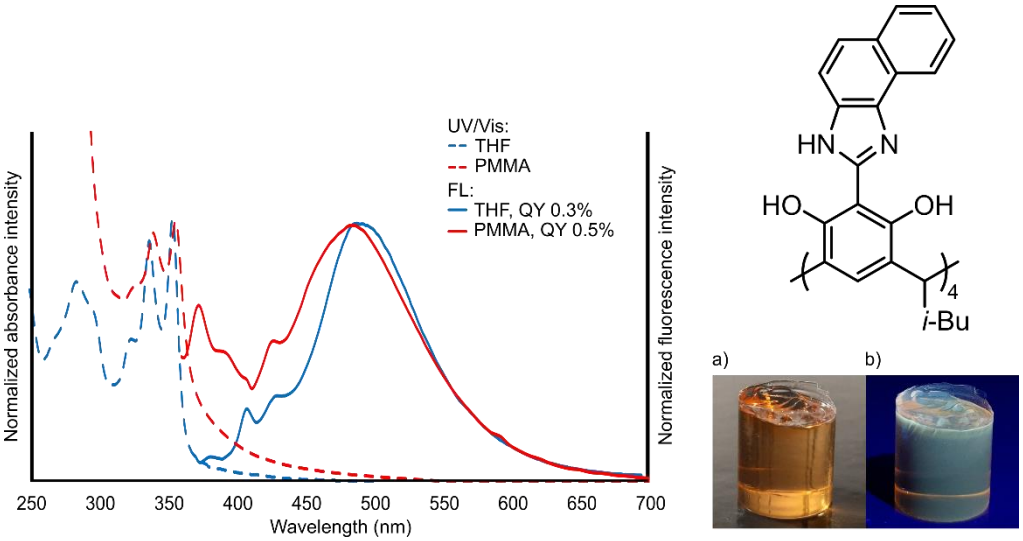


Figure S24. FL and UV properties of **1c**: FL and UV spectra in solution (blue line, C = $4.0 \cdot 10^{-6}$ M, λ_{ex} = 350 nm), FL and UV spectra in PMMA (red line, C = 0.2%, λ_{ex} = 350 nm); a) **PMMA-1c** under ambient light; b) **PMMA-1c** under UV light.

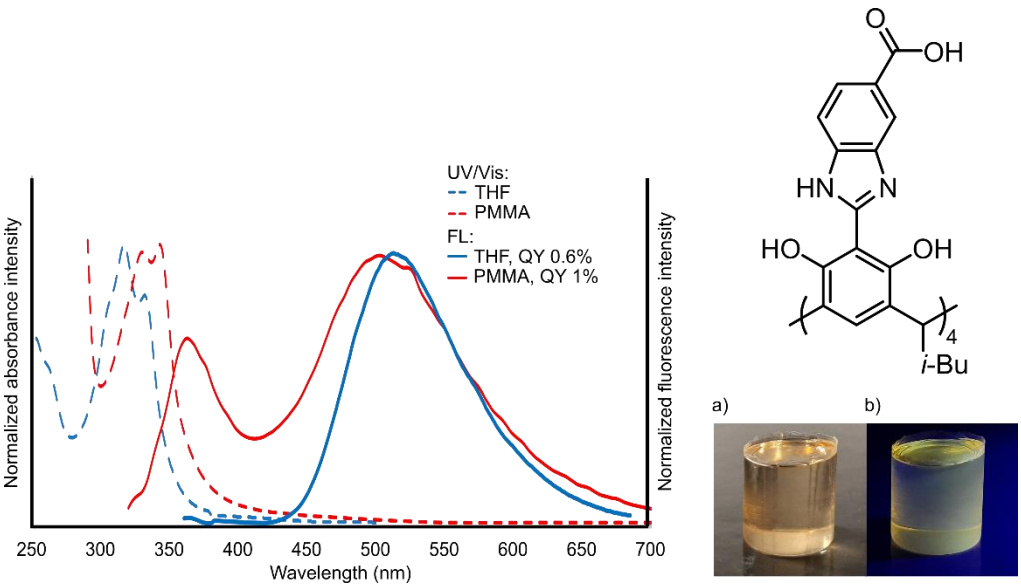


Figure S25. FL and UV properties of **1d**: FL and UV spectra in solution (blue line, C = $4.0 \cdot 10^{-6}$ M, λ_{ex} = 350 nm), FL and UV spectra in PMMA (red line, C = 0.2%, λ_{ex} = 310 nm); a) **PMMA-1d** under ambient light; b) **PMMA-1d** under UV light.

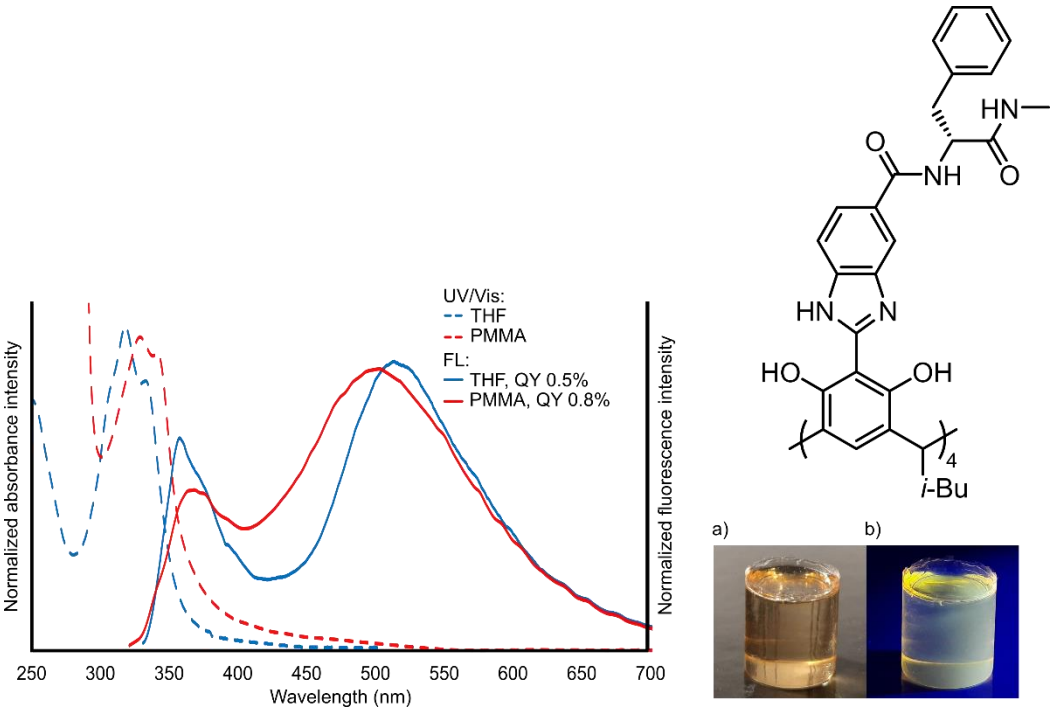


Figure S26. FL and UV properties of **D-1e**: FL and UV spectra in solution (blue line, C = $4.0 \cdot 10^{-6}$ M, λ_{ex} = 320 nm), FL and UV spectra in PMMA (red line, C = 0.2%, λ_{ex} = 320 nm); a) **PMMA-D-1e** under ambient light; b) **PMMA-D-1e** under UV light.

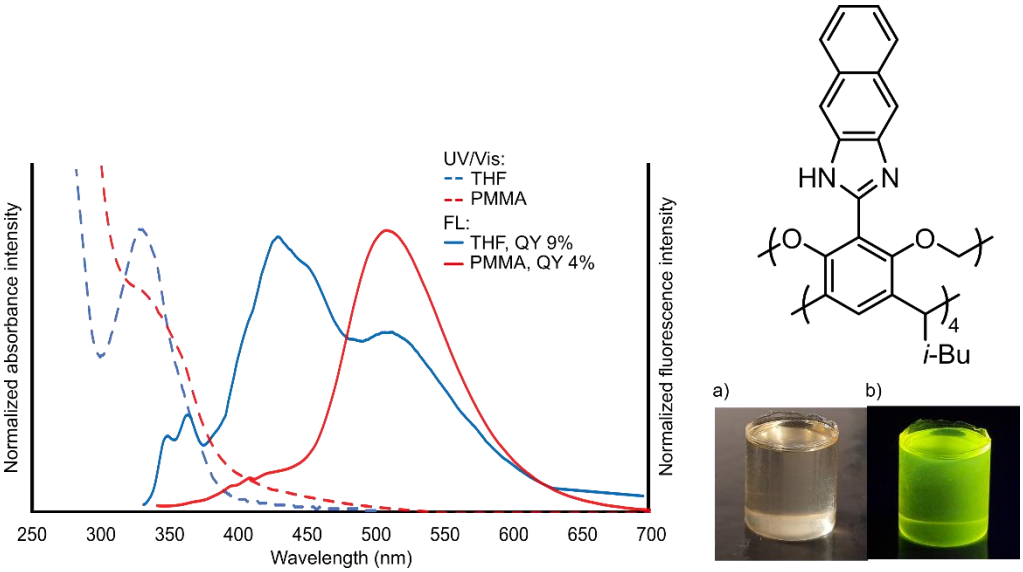


Figure S27. FL and UV properties of **2a**: FL and UV spectra in solution (blue line, C = $4.0 \cdot 10^{-6}$ M, λ_{ex} = 320 nm), FL and UV spectra in PMMA (red line, C = 0.2%, λ_{ex} = 320 nm); a) **PMMA-2a** under ambient light; b) **PMMA-2a** under UV light.

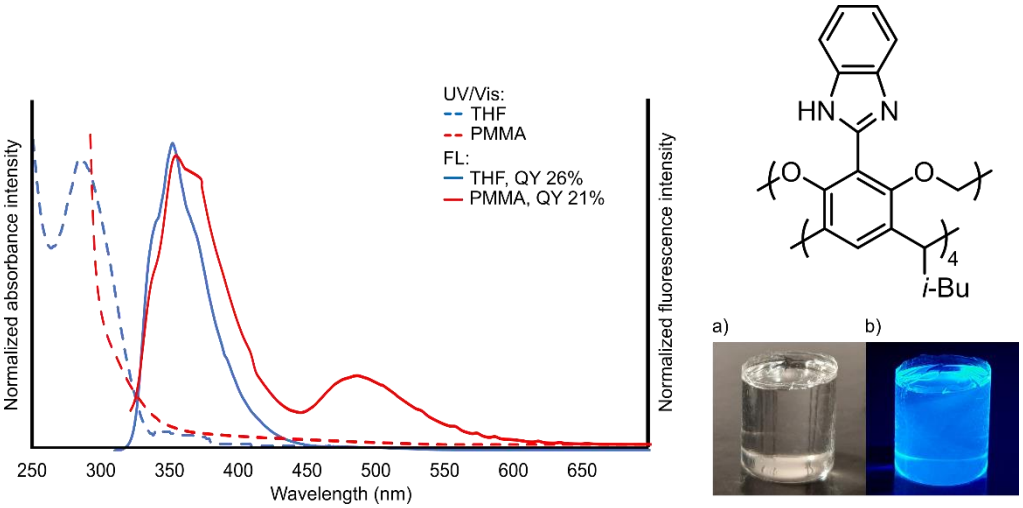


Figure S28. FL and UV properties of **2b**: FL and UV spectra in solution (blue line, C = $4.0 \cdot 10^{-6}$ M, λ_{ex} = 290 nm), FL and UV spectra in PMMA (red line, C = 0.2%, λ_{ex} =290 nm); a) **PMMA-2b** under ambient light; b) **PMMA-2b** under UV light.

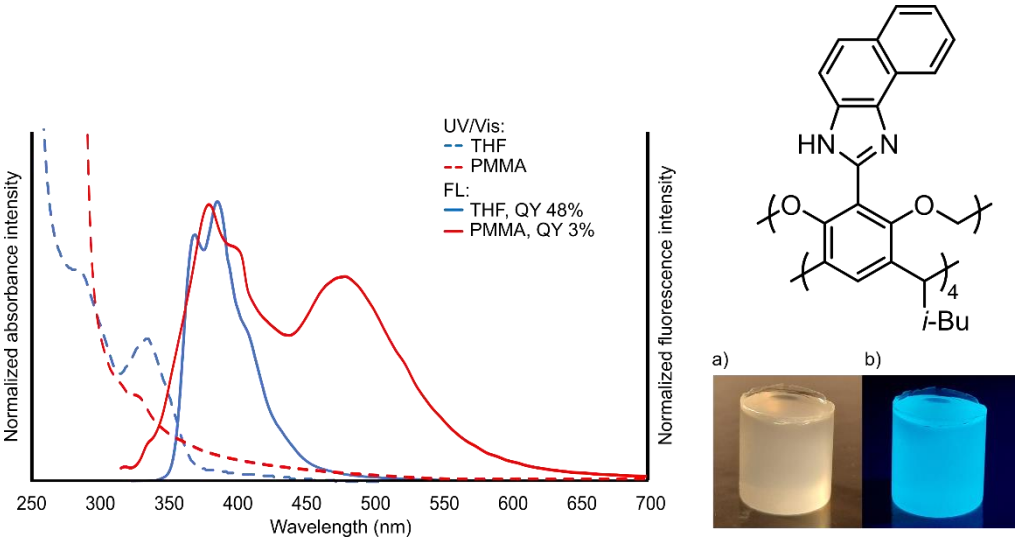


Figure S29. FL and UV properties of **2c**: FL and UV spectra in solution (blue line, C = $4.0 \cdot 10^{-6}$ M, λ_{ex} = 310 nm), FL and UV spectra in PMMA (red line, C = 0.2%, λ_{ex} = 310 nm); a) **PMMA-2c** under ambient light; b) **PMMA-2c** under UV light.

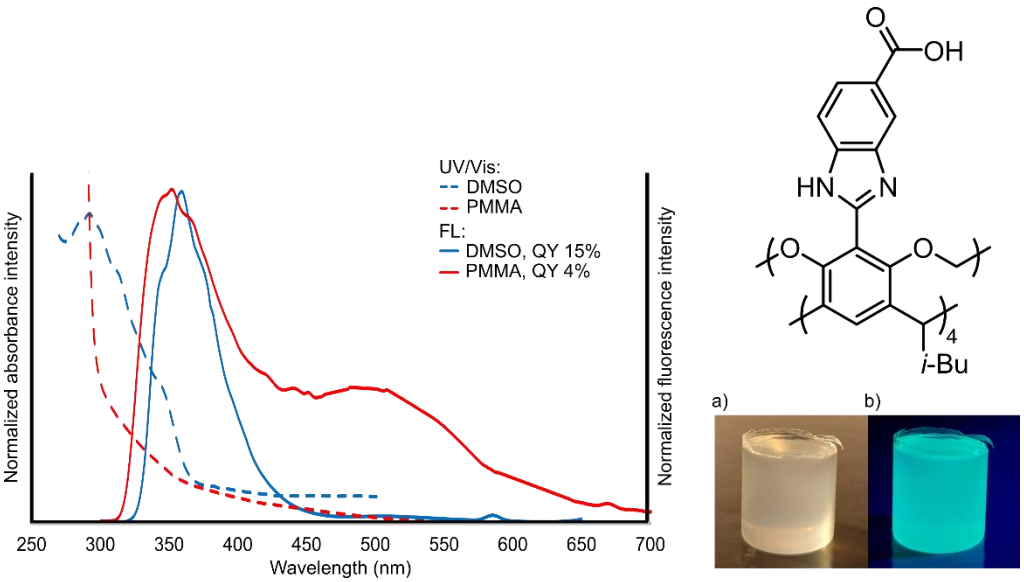


Figure S30. FL and UV properties of **2d**: FL and UV spectra in solution (blue line, C = $4.0 \cdot 10^{-6}$ M, λ_{ex} = 290 nm), FL and UV spectra in PMMA (red line, C = 0.2%, λ_{ex} = 290 nm); a) **PMMA-2d** under ambient light; b) **PMMA-2d** under UV light.

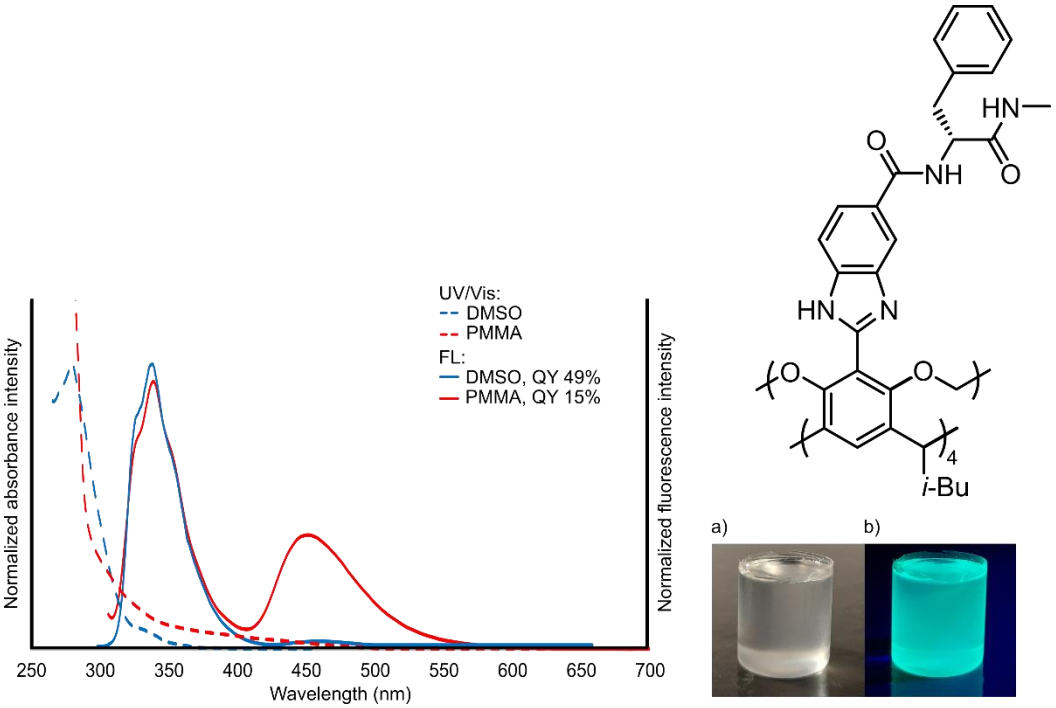


Figure S31. FL and UV properties of **D-2e**: FL and UV spectra in solution (blue line, C = $4.0 \cdot 10^{-6}$ M, λ_{ex} = 290 nm), FL and UV spectra in PMMA (red line, C = 0.2%, λ_{ex} = 290 nm); a) **PMMA-D-2e** under ambient light; b) **PMMA-D-2e** under UV light.

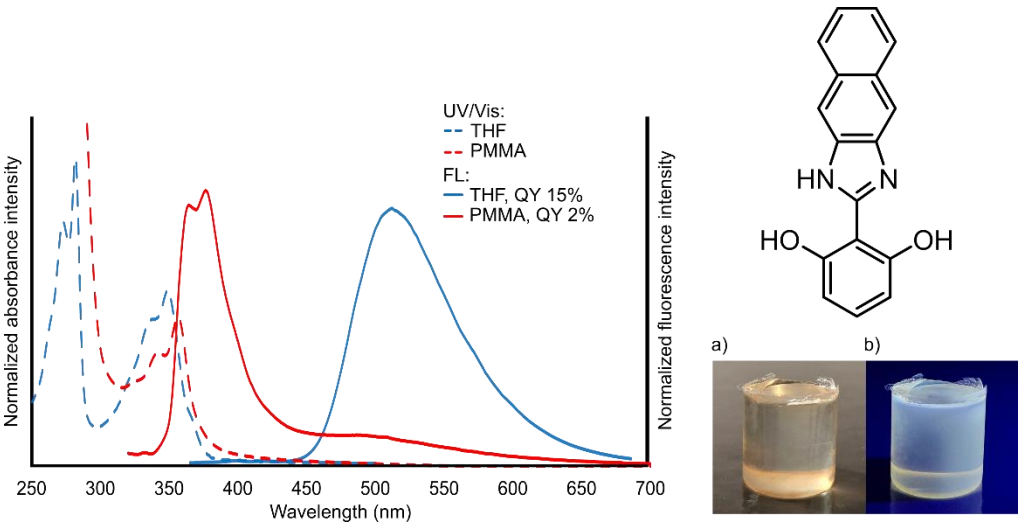


Figure S32. FL and UV properties of **3a**: FL and UV spectra in solution (blue line, C = $1.6 \cdot 10^{-5}$ M, λ_{ex} = 356 nm), FL and UV spectra in PMMA (red line, C = 0.2%, λ_{ex} = 310 nm); a) **PMMA-3a** under ambient light; b) **PMMA-3a** under UV light.

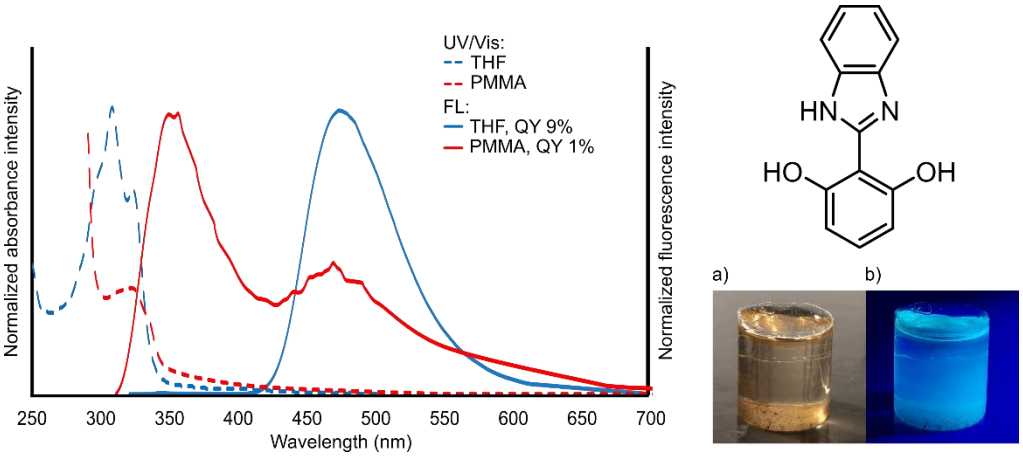


Figure S33. FL and UV properties of **3b**: FL and UV spectra in solution (blue line, C = $1.6 \cdot 10^{-5}$ M, λ_{ex} = 310 nm), FL and UV spectra in PMMA (red line, C = 0.2%, λ_{ex} = 310 nm); a) **PMMA-3b** under ambient light; b) **PMMA-3b** under UV light.

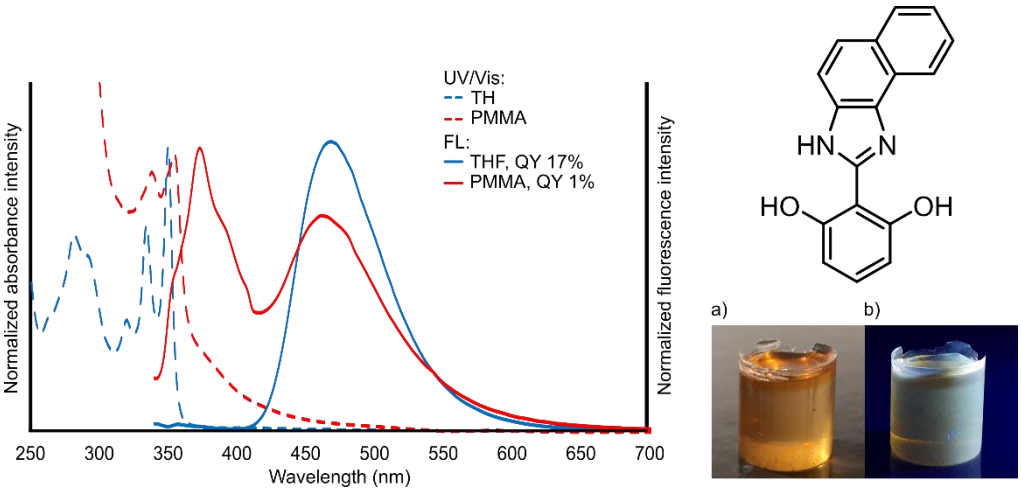


Figure S34. FL and UV properties of **3c**: FL and UV spectra in solution (blue line, C = $1.6 \cdot 10^{-5}$ M, λ_{ex} = 330 nm), FL and UV spectra in PMMA (red line, C = 0.2%, λ_{ex} = 330 nm); a) **PMMA-3c** under ambient light; b) **PMMA-3c** under UV light.

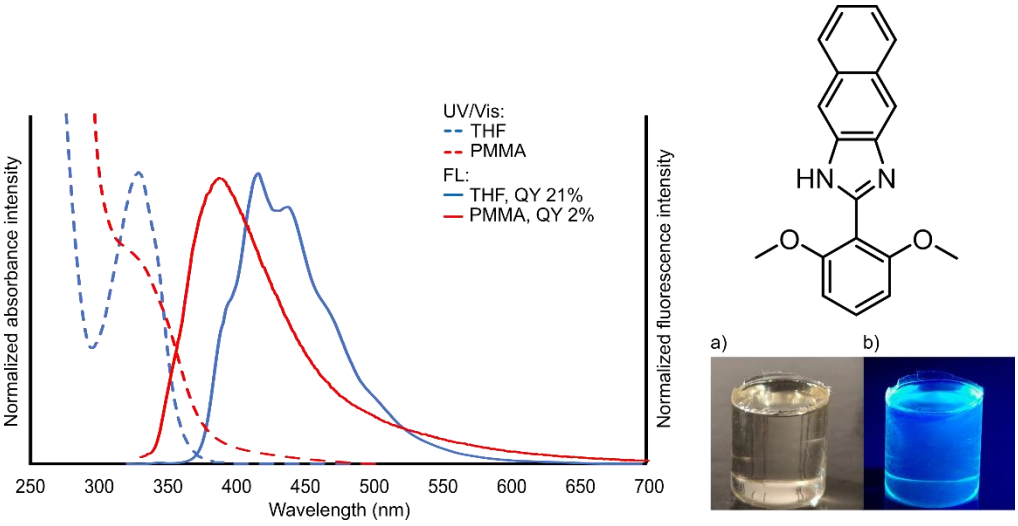


Figure S35. FL and UV properties of **4a**: FL and UV spectra in solution (blue line, C = $1.6 \cdot 10^{-5}$ M, λ_{ex} = 310 nm), FL and UV spectra in PMMA (red line, C = 0.2%, λ_{ex} = 310 nm); a) **PMMA-4a** under ambient light; b) **PMMA-4a** under UV light.

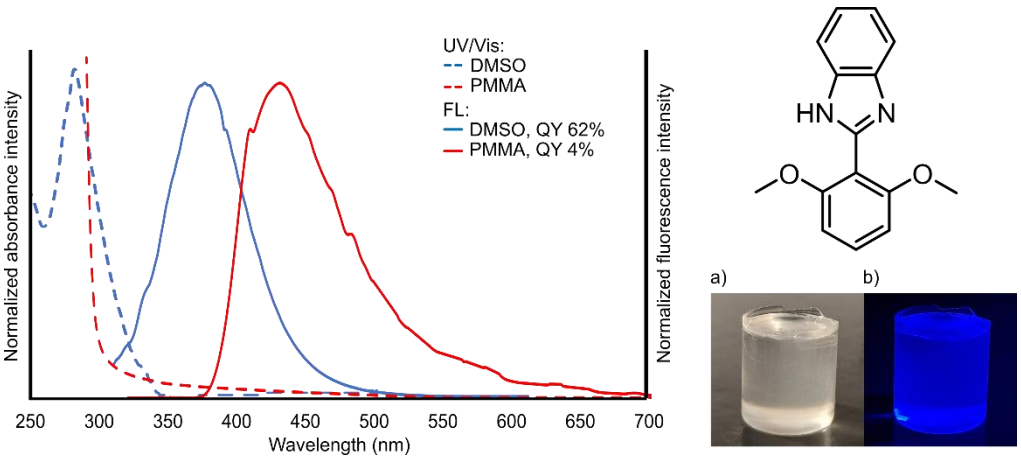


Figure S36. FL and UV properties of **4b**: FL and UV spectra in solution (blue line, C = $1.6 \cdot 10^{-5}$ M, λ_{ex} = 290 nm), FL and UV spectra in PMMA (red line, C = 0.2%, λ_{ex} = 290 nm); a) **PMMA-4b** under ambient light; b) **PMMA-4b** under UV light.

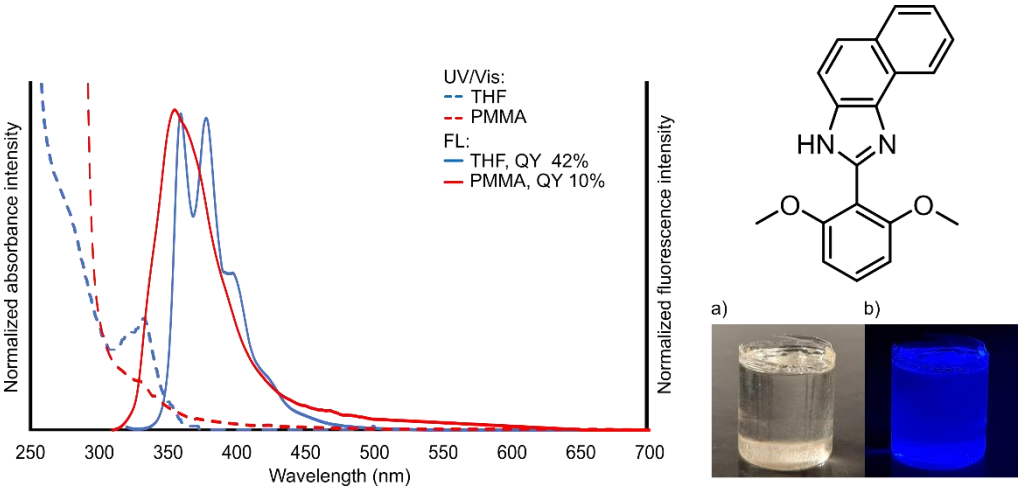
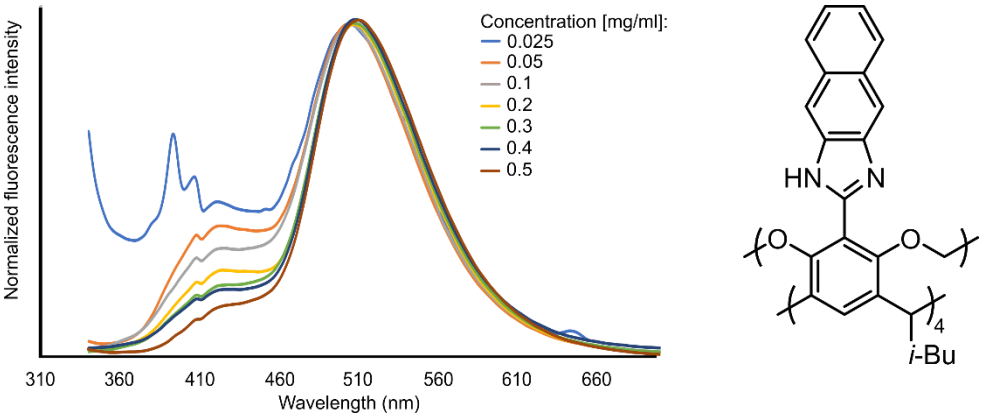


Figure S37. FL and UV properties of **4c**: FL and UV spectra in solution (blue line, C = $1.6 \cdot 10^{-5}$ M, λ_{ex} = 290 nm), FL and UV spectra in PMMA (red line, C = 0.2%, λ_{ex} = 290 nm); a) **PMMA-4c** under ambient light; b) **PMMA-4c** under UV light.

4. Aggregation studies

4.1 In PMMA

a)



b)

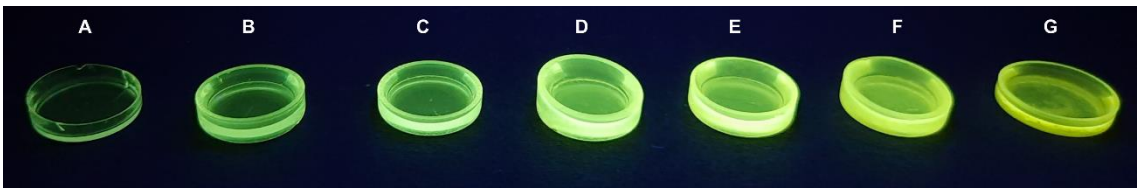


Figure S38. a) Normalized FL spectra of **PMMA-2a** with different concentration of **2a** in polymer, λ_{ex} = 320 nm; b) Photos of **PMMA-2a** with different amount of compound **2a**: A = 0.025 mg/ml, B = 0.05 mg/ml, C = 0.1 mg/ml, D = 0.2 mg/ml, E = 0.3 mg/ml, F= 0.4 mg/ml, g = 0.5 mg/ml.

4.2 In solution

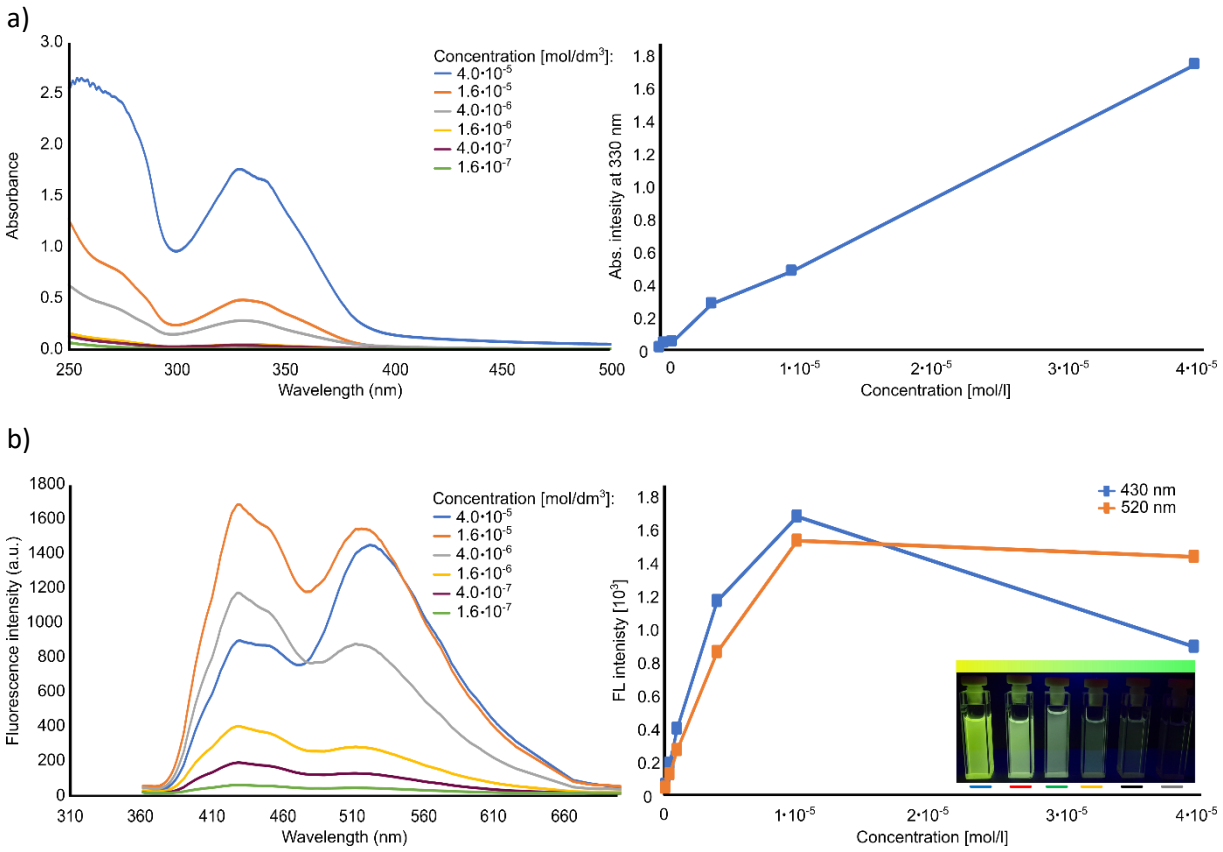
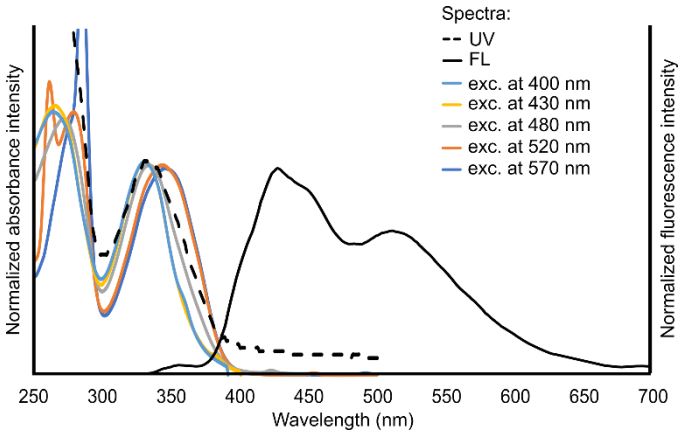
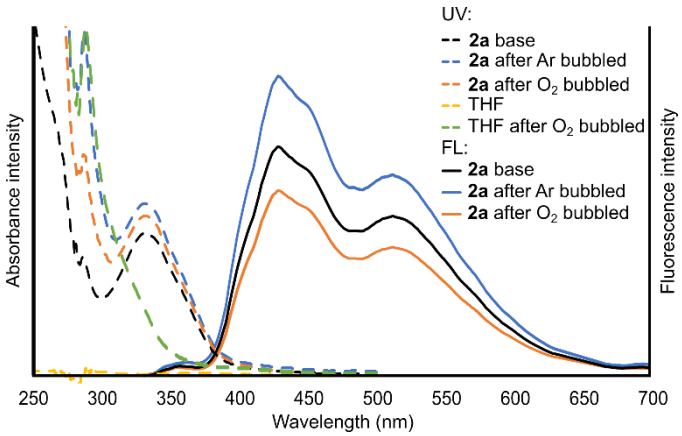


Figure S39. a) UV spectra of **2a** in THF; b) FL spectra of **2a** in THF, λ_{ex} = 320 nm.

a)



b)



c)

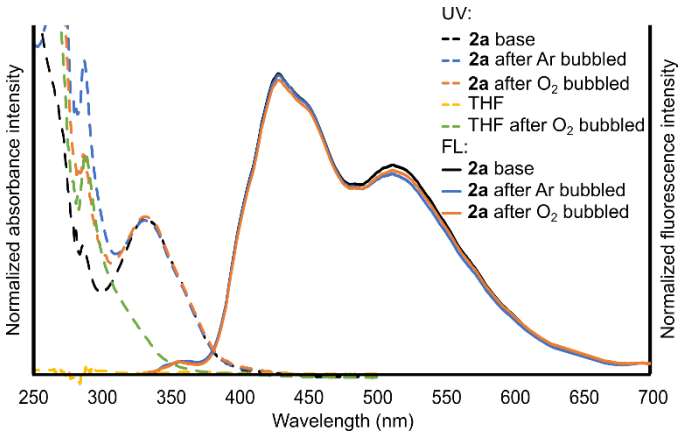


Figure S40. a) UV spectrum, FL spectrum λ_{ex} = 320 nm, and excitation spectra of **2a** in THF (C = $4.0 \cdot 10^{-6}$ M); b) UV spectra, FL spectra λ_{ex} = 320 nm spectra of **2a** in THF (C = $4.0 \cdot 10^{-6}$ M) after argon or oxygen bubbled; c) UV spectra, FL spectra λ_{ex} = 320 nm spectra of **2a** in THF (C = $4.0 \cdot 10^{-6}$ M) after argon or oxyden bubbled – normalized;

4.2.1 Aggregation study – DMSO/water or THF/water mixture

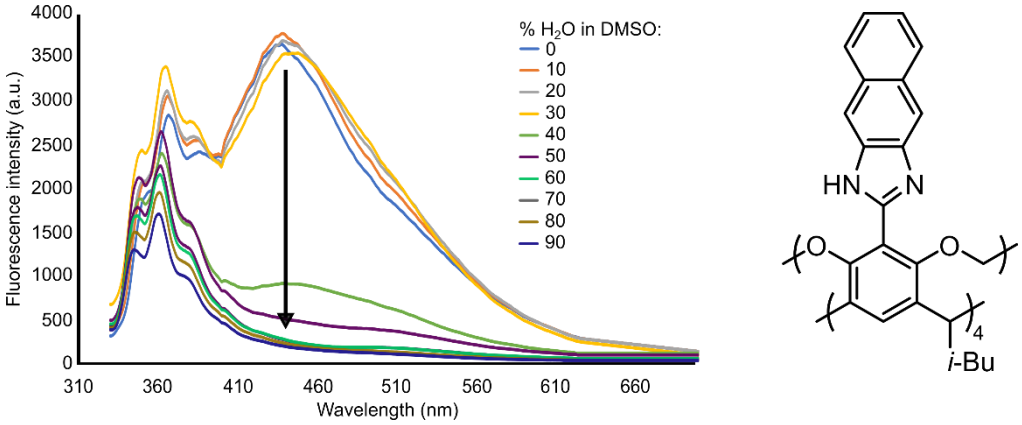
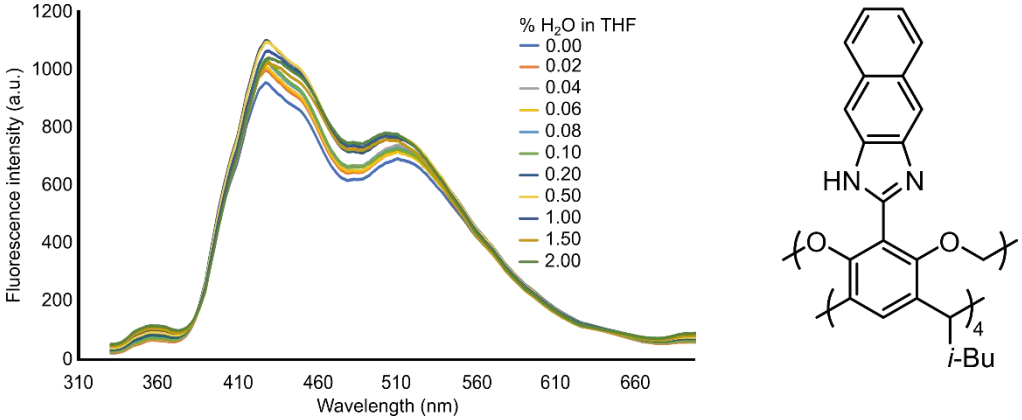


Figure S41. FL spectra of **2a** in DMSO/water mixture (C = $4.0 \cdot 10^{-6}$ M, λ_{ex} = 320 nm).

a)



b)

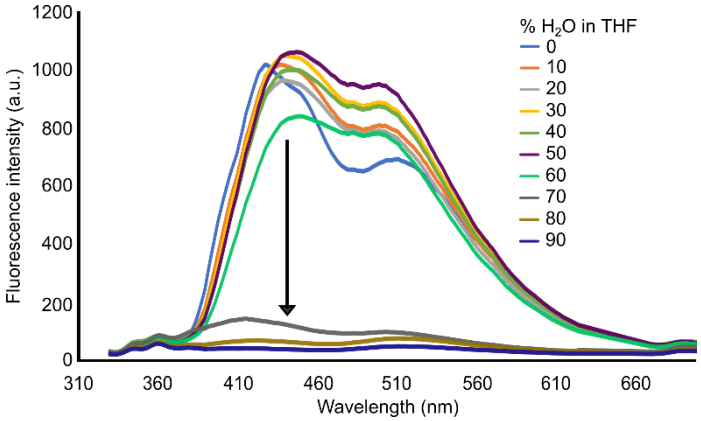


Figure S42. FL spectra of **2a** in THF/water mixture (C = $4.0 \cdot 10^{-6}$ M, λ_{ex} = 320 nm).

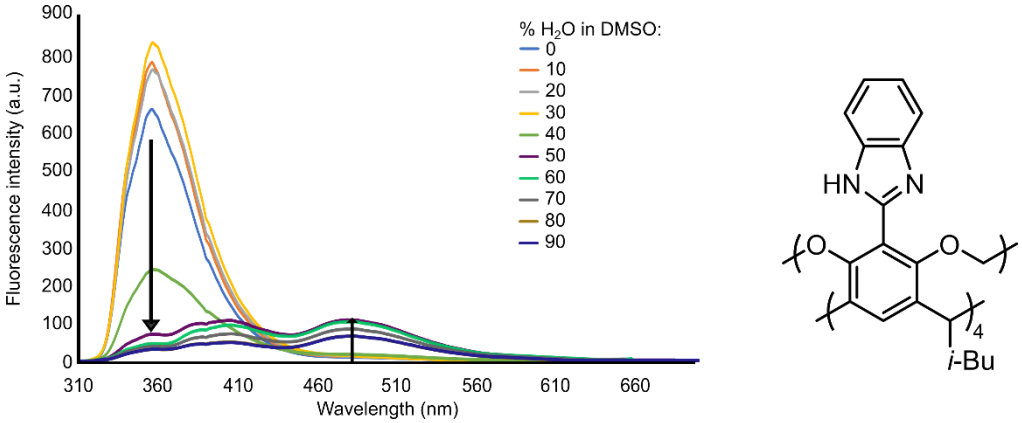


Figure S43. FL spectra of **2b** in DMSO/water mixture (C = $4.0 \cdot 10^{-6}$ M, λ_{ex} = 290 nm).

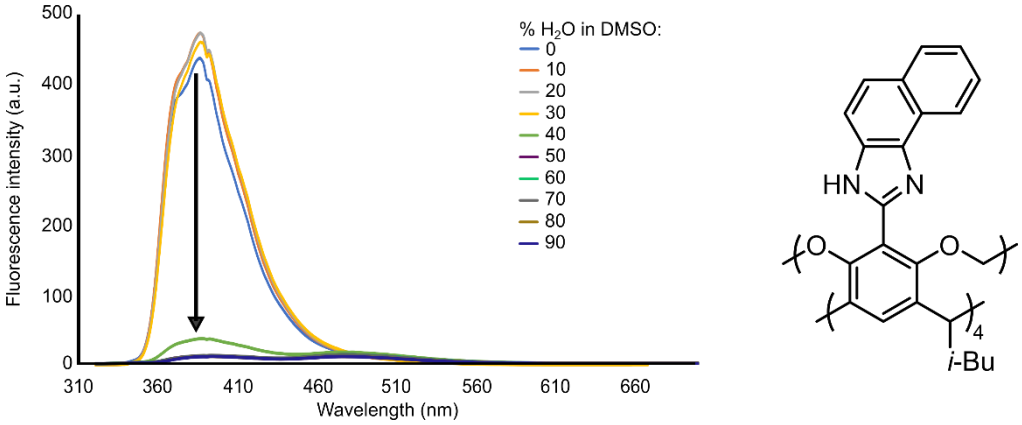


Figure S44. FL spectra of **2c** in DMSO/water mixture (C = $4.0 \cdot 10^{-6}$ M, λ_{ex} = 310 nm).

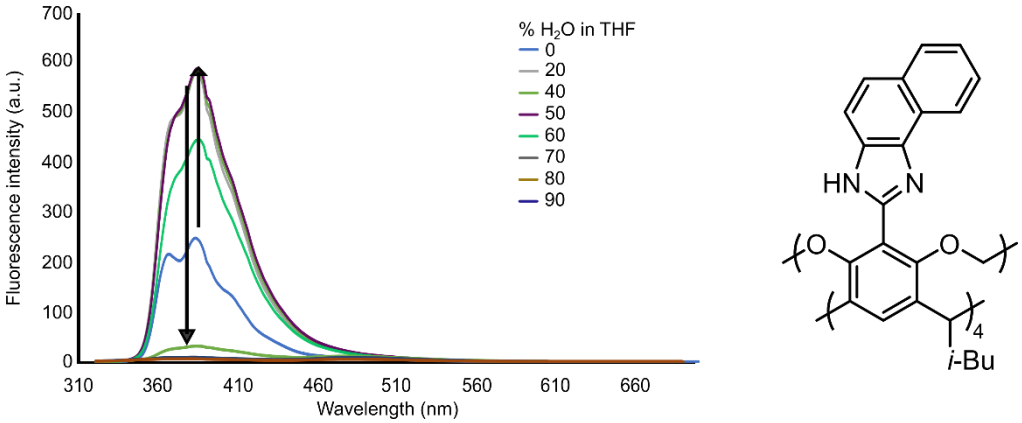


Figure S45. FL spectra of **2c** in THF/water mixture (C = $4.0 \cdot 10^{-6}$ M, λ_{ex} = 310 nm).

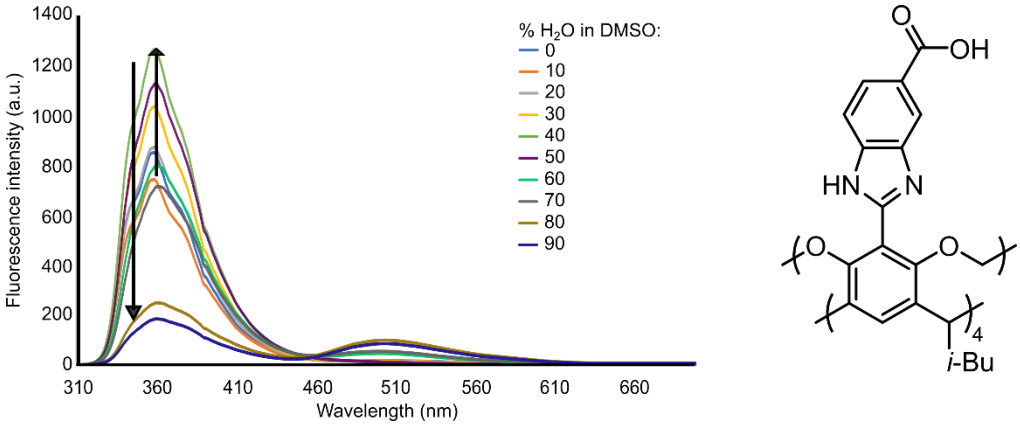


Figure S46. FL spectra of **2d** in DMSO/water mixture (C = $4.0 \cdot 10^{-6}$ M, λ_{ex} = 290 nm).

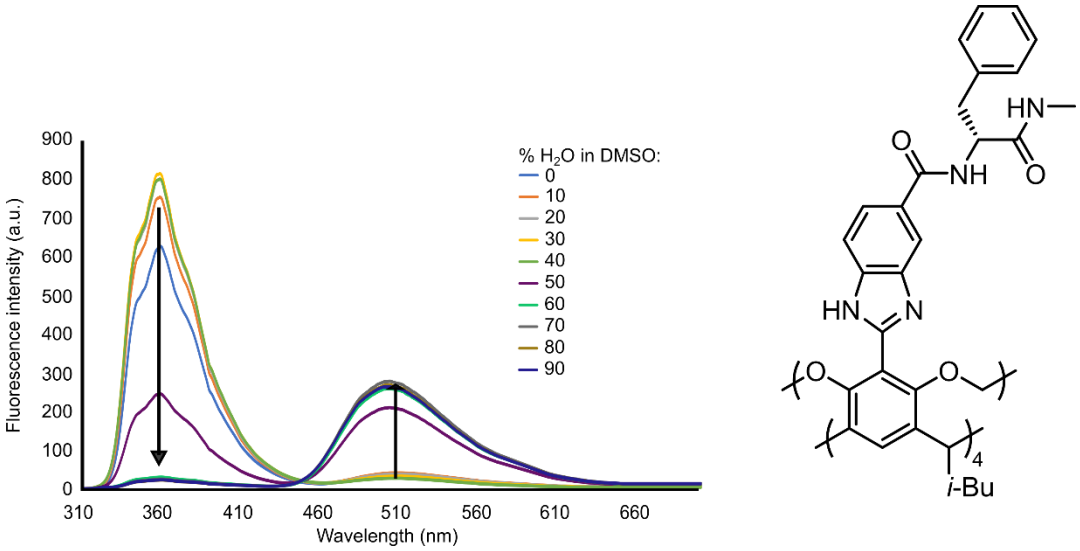


Figure S47. FL spectra of **D-2e** in DMSO/water mixture (C = $4.0 \cdot 10^{-6}$ M, λ_{ex} = 290 nm).

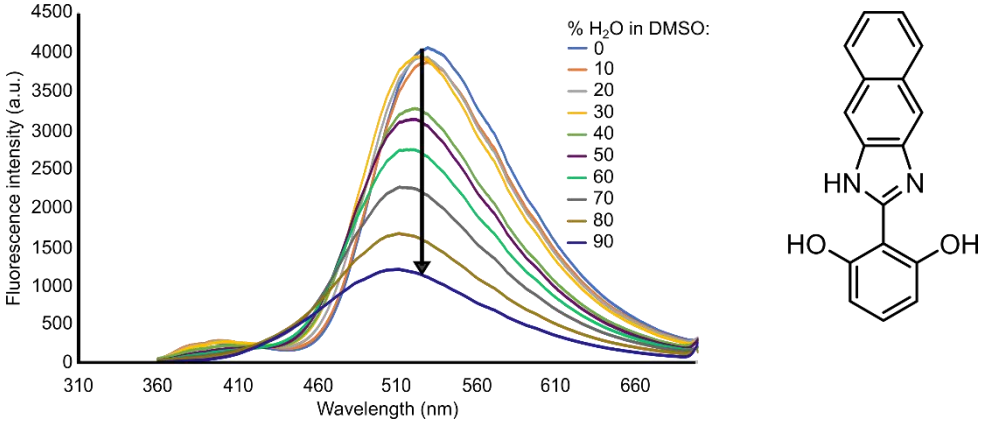
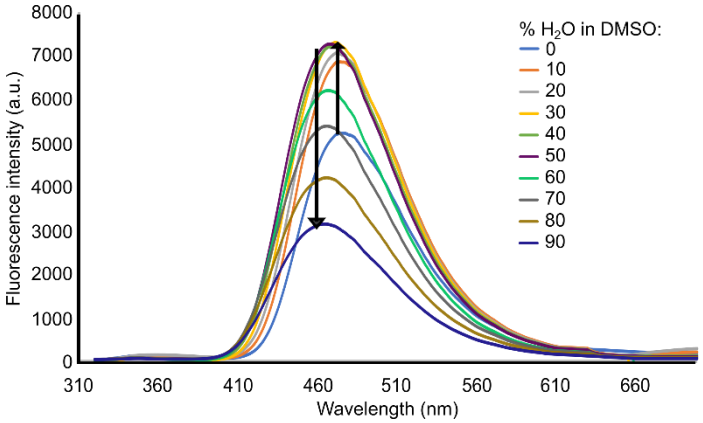


Figure S48. FL spectra of **3a** in DMSO/water mixture (C = $1.6 \cdot 10^{-5}$ M, λ_{ex} = 356 nm).



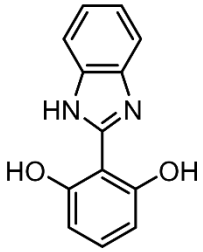
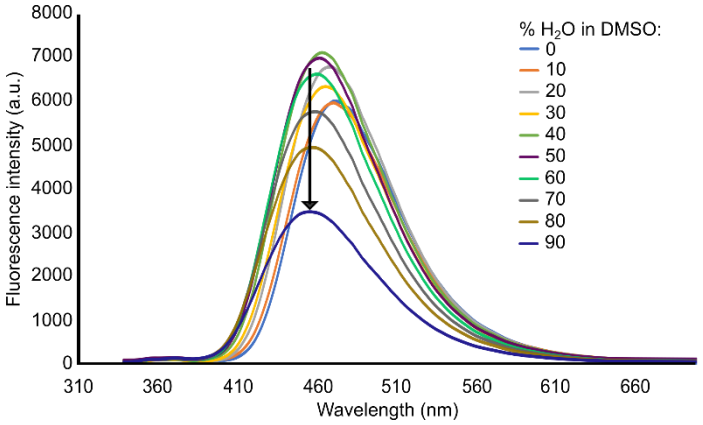


Figure S49. FL spectra of **3b** in DMSO/water mixture (C = $1.6 \cdot 10^{-5}$ M, λ_{ex} = 310 nm).



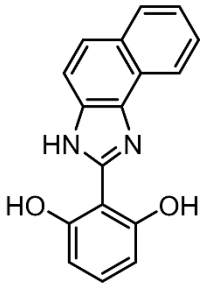
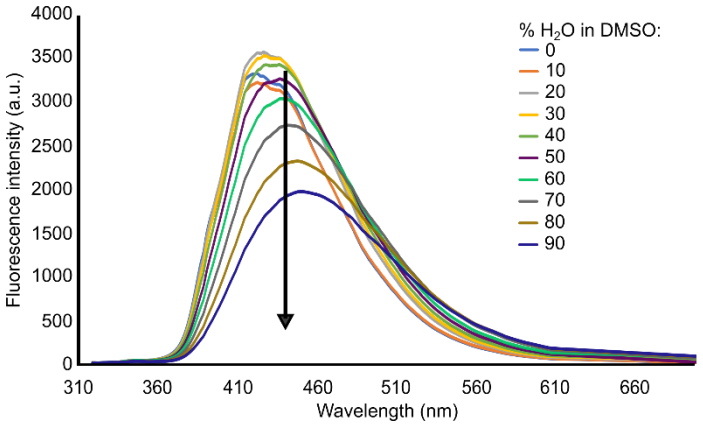


Figure S50. FL spectra of **3c** in DMSO/water mixture (C = $1.6 \cdot 10^{-5}$ M, λ_{ex} = 330 nm).



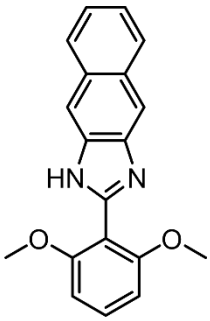


Figure S51. FL spectra of **4a** in DMSO/water mixture (C = $1.6 \cdot 10^{-5}$ M, λ_{ex} = 310 nm).

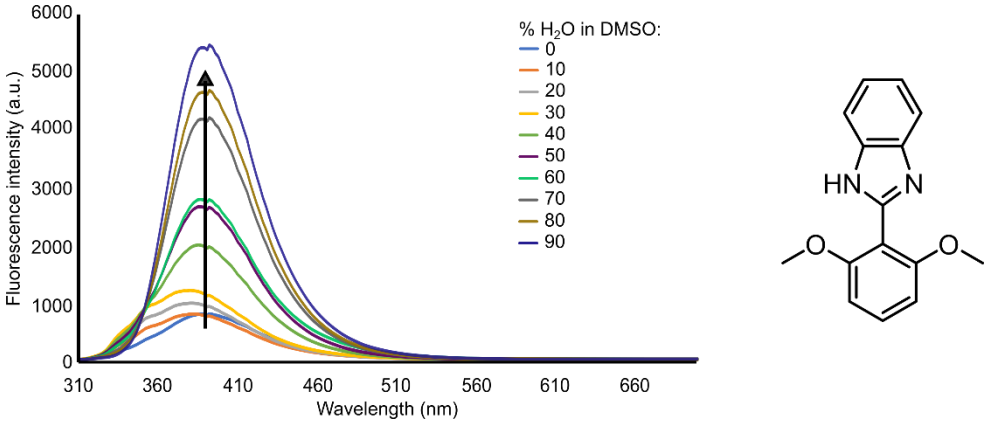


Figure S52. FL spectra of **4b** in DMSO/water mixture (C = $1.6 \cdot 10^{-5}$ M, λ_{ex} = 290 nm).

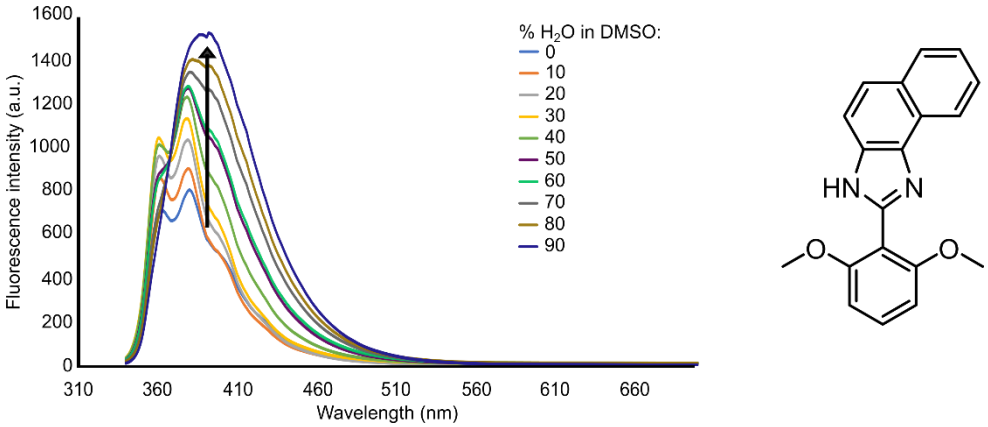


Figure S53. FL spectra of **4c** in DMSO/water mixture (C = $1.6 \cdot 10^{-5}$ M, λ_{ex} = 330 nm).

5. Theoretical calculations

5.1 Computational methods for tetramers

All calculations for cavitands in its neutral (**N**-tautomer) and charged (**C**-tautomer) forms were performed within the density functional theory (DFT) approach using Gaussian 16 program suite.[2] Geometry was optimized with the B3LYP functional, employing the 6-31++G(D,P) basis set. Solvent effects were considered within the SMD model approach to model the interaction with the solvent. Vertical excitation energies were determined at the WB97XD/6-31++G(D,P) theory level by means of the time-dependent DFT (TD DFT) approach. The UV absorption spectra were next simulated by overlapping Gaussian functions for each transition where the width of the band at 1/e height is fixed at 0.2 eV and the resulting intensities of the combined spectra were scaled to the experimental values.

Atomic coordinates for calculated geometries of cavitands (solvent: THF)

N-tautomer

Number of imaginary frequencies 0

Symbol	X	Y	Z
O	-4.45828600	-1.61132200	-2.12474402
O	3.12847000	3.57095600	-2.09650602
O	-1.61132200	4.45828600	-2.12474402
O	-3.57095600	3.12847000	-2.09650602
O	3.57095600	-3.12847000	-2.09650602
O	4.45828600	1.61132200	-2.12474402
O	1.61132200	-4.45828600	-2.12474402
O	-3.12847000	-3.57095600	-2.09650602
C	3.67912200	2.48906300	-1.33455702
H	2.88348200	1.94721400	-0.81863402
H	4.36859800	2.95379300	-0.63110902
C	-2.48906300	3.67912200	-1.33455702
H	-2.95379300	4.36859800	-0.63110902
H	-1.94721400	2.88348200	-0.81863402
C	2.48906300	-3.67912200	-1.33455702
H	1.94721400	-2.88348200	-0.81863402
H	2.95379300	-4.36859800	-0.63110902
C	-3.67912200	-2.48906300	-1.33455702
H	-2.88348200	-1.94721400	-0.81863402
H	-4.36859800	-2.95379300	-0.63110902
C	-2.71510600	1.76675600	-3.88683102
C	-0.50242500	-2.61777400	-4.47467902
H	-0.40478000	-2.08907900	-5.41952302
C	3.16353300	0.64033400	-3.88608402
C	-2.01266100	2.96285100	-4.50537902
H	-2.61737300	3.86334700	-4.36736202
H	-1.89825200	2.79100300	-5.57901202
C	3.84063800	0.50242500	-2.66674602
C	1.76675600	2.71510600	-3.88683102
C	-3.84063800	-0.50242500	-2.66674602
C	-2.61777400	0.50242500	-4.47467902
H	-2.08907900	0.40478000	-5.41952302
C	1.87898200	3.40384800	-2.67198602
C	-0.50242500	3.84063800	-2.66674602
C	0.50242500	-3.84063800	-2.66674602
C	2.61777400	-0.50242500	-4.47467902
H	2.08907900	-0.40478000	-5.41952302
C	-3.40384800	1.87898200	-2.67198602
C	-1.76675600	-2.71510600	-3.88683102
C	2.71510600	-1.76675600	-3.88683102
C	0.50242500	2.61777400	-4.47467902
H	0.40478000	2.08907900	-5.41952302
C	3.98338900	-0.75534900	-2.03770302
C	-2.96285100	-2.01266100	-4.50537902
H	-3.86334700	-2.61737300	-4.36736202
H	-2.79100300	-1.89825200	-5.57901202
C	0.64033400	-3.16353300	-3.88608402
C	-1.87898200	-3.40384800	-2.67198602
C	-0.75534900	-3.98338900	-2.03770302
C	-0.64033400	3.16353300	-3.88608402
C	2.96285100	2.01266100	-4.50537902
H	3.86334700	2.61737300	-4.36736202
H	2.79100300	1.89825200	-5.57901202
C	-3.98338900	0.75534900	-2.03770302

C	-3.16353300	-0.64033400	-3.88608402
C	2.01266100	-2.96285100	-4.50537902
H	2.61737300	-3.86334700	-4.36736202
H	1.89825200	-2.79100300	-5.57901202
C	3.40384800	-1.87898200	-2.67198602
C	0.75534900	3.98338900	-2.03770302
C	0.88605800	4.70389700	-0.75474202
C	0.53200500	5.49578800	1.22210398
C	1.79888300	6.01453800	0.80167598
C	0.02268400	5.82271900	2.46796398
C	2.56464200	6.85019400	1.58978898
C	0.77656400	6.67708400	3.30924198
H	-0.93625100	5.43454900	2.79997498
C	2.05573300	7.19484000	2.86784098
H	3.52362100	7.23803800	1.25836298
C	4.70389700	-0.88605800	-0.75474202
C	5.49578800	-0.53200500	1.22210398
C	6.01453800	-1.79888300	0.80167598
C	5.82271900	-0.02268400	2.46796398
C	6.85019400	-2.56464200	1.58978898
C	6.67708400	-0.77656400	3.30924198
H	5.43454900	0.93625100	2.79997498
C	7.19484000	-2.05573300	2.86784098
H	7.23803800	-3.52362100	1.25836298
C	-0.88605800	-4.70389700	-0.75474202
C	-0.53200500	-5.49578800	1.22210398
C	-1.79888300	-6.01453800	0.80167598
C	-0.02268400	-5.82271900	2.46796398
C	-2.56464200	-6.85019400	1.58978898
C	-0.77656400	-6.67708400	3.30924198
H	0.93625100	-5.43454900	2.79997498
C	-2.05573300	-7.19484000	2.86784098
H	-3.52362100	-7.23803800	1.25836298
C	-4.70389700	0.88605800	-0.75474202
C	-5.49578800	0.53200500	1.22210398
C	-6.01453800	1.79888300	0.80167598
C	-5.82271900	0.02268400	2.46796398
C	-6.85019400	2.56464200	1.58978898
C	-6.67708400	0.77656400	3.30924198
H	-5.43454900	-0.93625100	2.79997498
C	-7.19484000	2.05573300	2.86784098
H	-7.23803800	3.52362100	1.25836298
N	1.98267400	5.48795800	-0.46119202
N	-0.00035300	4.68839400	0.22519298
C	0.30209800	7.04925800	4.60471998
C	2.78249400	8.05334200	3.74785598
C	2.28922300	8.38742200	4.98850698
H	2.85929500	9.04183600	5.64225198
C	1.03335100	7.87920900	5.42289398
H	0.65431000	8.14951400	6.40456398
H	-0.65771200	6.65859600	4.93401798
H	3.74249200	8.44139600	3.41590798
N	4.68839400	0.00035300	0.22519298
N	5.48795800	-1.98267400	-0.46119202
C	7.04925800	-0.30209800	4.60471998
C	7.87920900	-1.03335100	5.42289398
H	8.14951400	-0.65431000	6.40456398
C	8.38742200	-2.28922300	4.98850698
H	9.04183600	-2.85929500	5.64225198
C	8.05334200	-2.78249400	3.74785598
H	6.65859600	0.65771200	4.93401798
H	8.44139600	-3.74249200	3.41590798

C	-0.30209800	-7.04925800	4.60471998	C	-7.04925800	0.30209800	4.60471998
C	-1.03335100	-7.87920900	5.42289398	C	-7.87920900	1.03335100	5.42289398
H	-0.65431000	-8.14951400	6.40456398	C	-8.38742200	2.28922300	4.98850698
C	-2.28922300	-8.38742200	4.98850698	C	-8.05334200	2.78249400	3.74785598
H	-2.85929500	-9.04183600	5.64225198	H	-8.44139600	3.74249200	3.41590798
C	-2.78249400	-8.05334200	3.74785598	H	-9.04183600	2.85929500	5.64225198
H	-3.74249200	-8.44139600	3.41590798	H	-8.14951400	0.65431000	6.40456398
H	0.65771200	-6.65859600	4.93401798	H	-6.65859600	-0.65771200	4.93401798
N	0.00035300	-4.68839400	0.22519298	H	2.80615500	5.57668500	-1.04076002
N	-1.98267400	-5.48795800	-0.46119202	H	5.57668500	-2.80615500	-1.04076002
N	-4.68839400	-0.00035300	0.22519298	H	-2.80615500	-5.57668500	-1.04076002
N	-5.48795800	1.98267400	-0.46119202	H	-5.57668500	2.80615500	-1.04076002

C-tautomer

Number of imaginary frequencies 0

Symbol	X	Y	Z				
O	-2.40668600	4.07018100	-1.98561700	H	-2.37080200	-2.47660700	-0.73745800
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O	4.08728300	2.44285500	-1.92145200	C	-3.06313700	3.12771400	-1.19119300
O	2.39125500	4.11123200	-1.98862300	H	-2.36331800	2.42442900	-0.73287700
O	-2.38348300	-4.11270300	-2.00549100	H	-3.62209300	3.68839100	-0.44134500
O	2.41811500	-4.06997500	-1.98574800	C	1.22183800	3.00216900	-3.77649600
O	-4.07882300	-2.44383800	-1.94041000	C	-2.67639400	-0.01849100	-4.30395200
O	-4.08396400	2.38293800	-1.91786300	H	-2.13049000	-0.01408800	-5.24378100
C	3.07358800	-3.13277100	-1.18382100	C	1.23909900	-2.97637300	-3.77311000
H	2.37364200	-2.43221900	-0.72235000	C	2.54458000	2.54271400	-4.36119200
H	3.63241900	-3.69775500	-0.43740200	H	3.30089900	3.32122900	-4.22756900
C	3.06280300	3.17985100	-1.19259800	H	2.42282900	2.36975600	-5.43374200
H	3.61904000	3.75033300	-0.44828500	C	1.21488400	-3.69208600	-2.57003700
H	2.37279700	2.47103000	-0.72709900	C	3.01988100	-1.20761600	-3.70886800
C	-3.05808100	-3.18388600	-1.20987800	C	-1.20349300	3.69519900	-2.57227900

C	0.00187800	2.65284800	-4.36413100
H	0.00673800	2.09750900	-5.29879700
C	3.73835100	-1.19481000	-2.50800500
C	3.73510100	1.24631700	-2.51536400
C	-3.72213100	-1.24702500	-2.53173400
C	0.01633600	-2.65126100	-4.36788800
H	0.01472700	-2.09383600	-5.30126000
C	1.19226300	3.71930800	-2.57387300
C	-3.00341900	1.20830700	-3.72046800
C	-1.20557500	-3.00300100	-3.78550000
C	2.69479400	0.01970500	-4.29222200
H	2.15184600	0.01630500	-5.23375800
C	0.01818900	-4.09460200	-1.95813700
C	-2.54058700	2.50506900	-4.36188100
H	-3.30444600	3.27659200	-4.22969700
H	-2.41488000	2.33426600	-5.43432400
C	-2.99888400	-1.25080600	-3.72936800
C	-3.72465600	1.19380200	-2.52138600
C	-4.15096700	-0.02920600	-1.93398800
C	3.01513500	1.25107300	-3.71495700
C	2.55874200	-2.50293200	-4.35410800
H	3.32107800	-3.27551700	-4.21952700
H	2.43770000	-2.33053400	-5.42682800
C	-0.00895000	4.09512000	-1.95575400
C	-1.22373600	2.97962000	-3.77545500
C	-2.52603400	-2.54215100	-4.37472000
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H	-2.39981800	-2.36756300	-5.44648700
C	-1.18075100	-3.72205400	-2.58406200
C	4.16353400	0.02782900	-1.91859200
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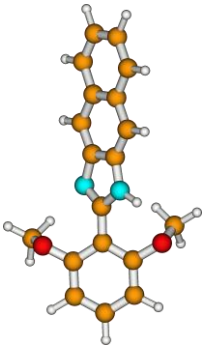
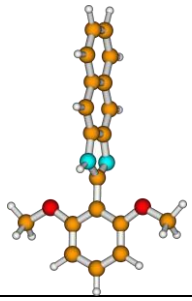
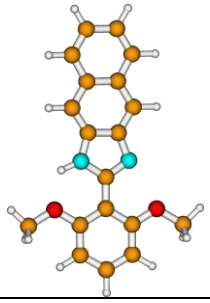
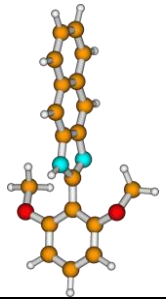
C	6.44400400	-0.66531600	0.86762300
C	7.21911700	1.49344600	1.72417700
C	7.19195700	-1.39268000	1.76687900
C	8.00441200	0.78075000	2.66462300
H	7.22418400	2.57846400	1.70561300
C	7.99004300	-0.66730700	2.68691200
H	7.17704900	-2.47763700	1.78058400
C	0.02819100	-4.83575600	-0.66367400
C	0.17689900	-5.18255700	1.43763400
C	-0.07493400	-6.42974100	0.74722900
C	0.31212300	-5.14655900	2.81958700
C	-0.18774200	-7.62255800	1.44929500
C	0.20134500	-6.35471300	3.55200800
H	0.50050600	-4.21188600	3.34425200
C	-0.05081300	-7.60526300	2.85956300
H	-0.37660400	-8.56285500	0.93550700
C	-5.05305000	-0.03420600	-0.78531200
C	-6.43897500	-0.75497900	0.83600800
C	-6.43063700	0.66447000	0.85257100
C	-7.19535600	-1.49458500	1.71798300
C	-7.17907400	1.39176500	1.75135700
C	-7.98076600	-0.78172900	2.65859500
H	-7.19657900	-2.57964200	1.70326500
C	-7.97204600	0.66647000	2.67567200
H	-7.16771700	2.47680100	1.76172200
C	-0.02354000	4.83592100	-0.66101700
C	-0.10392500	5.17514000	1.44425400
C	-0.02341800	6.43842000	0.74309400
C	-0.17207000	5.13133100	2.83098500
C	-0.01456400	7.64050600	1.43856700

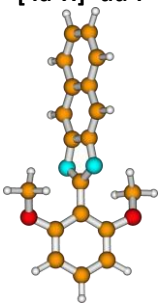
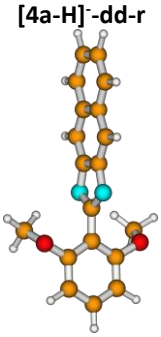
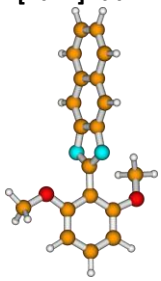
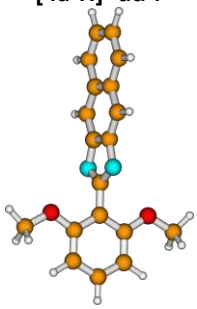
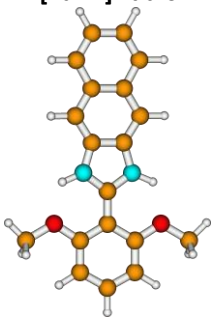
C	-0.16517900	6.34823400	3.55703700
H	-0.23267600	4.18460300	3.36419600
C	-0.08575700	7.61549400	2.85353200
H	0.04452800	8.59302600	0.91612100
N	5.57205100	-1.05060500	-0.14597000
N	5.59021600	1.12475600	-0.17605800
C	8.82208200	1.47024600	3.61014500
C	8.79391900	-1.34381500	3.65311400
C	9.56787900	-0.64168700	4.54697600
H	10.17306100	-1.17246100	5.27618100
C	9.58236800	0.78037700	4.52496200
H	10.19792000	1.32111500	5.23798600
H	8.82970200	2.55674900	3.59241100
H	8.78067200	-2.43032000	3.66846300
N	0.23948600	-4.17312900	0.49684800
N	-0.16559400	-6.16732600	-0.60553000
C	0.33210000	-6.38318500	4.97517600
C	0.22422200	-7.55742200	5.68725500
H	0.32749000	-7.55103200	6.76928300
C	-0.02333900	-8.78380300	5.00824700
H	-0.10753700	-9.70693700	5.57587400
C	-0.15569400	-8.80010300	3.63727000
H	0.52118600	-5.44545800	5.49394300
H	-0.34465800	-9.73735400	3.11775700
C	-8.79242000	-1.47099500	3.60893200
C	-9.55178600	-0.78092000	4.52473100
H	-10.16284800	-1.32165600	5.24159700
C	-9.54233700	0.64107500	4.54220600
H	-10.14581400	1.17220500	5.27255000
C	-8.77407200	1.34321100	3.64323900
H	-8.76487800	2.42980400	3.65478900
H	-8.79745900	-2.55755100	3.59488200
N	-5.57371700	-1.12631500	-0.18819600
N	-5.56078000	1.04964700	-0.16260500
N	-0.10216400	4.15945700	0.50722100
N	0.02905200	6.18109300	-0.61303900
C	-0.23758800	6.36999700	4.98452200
C	-0.23449000	7.55298700	5.69004400
C	-0.15648900	8.79577100	5.00023500
C	-0.08393600	8.81890300	3.62501600
H	-0.02450500	9.76845700	3.09698400
H	-0.15457200	9.72588900	5.56264400
H	-0.29175300	7.54146900	6.77545000
H	-0.29709400	5.41987300	5.51168400
H	5.36905300	-1.99450900	-0.45554900
H	-5.36095500	1.99344900	-0.47452500
H	5.39262000	2.06340600	-0.50518800
H	-5.37440000	-2.06492900	-0.51683900

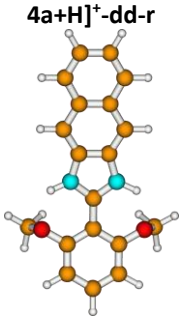
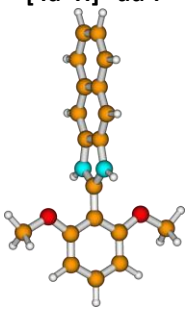
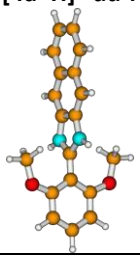
5.2 Computational methods for monomers

Photophysical properties of **4a** in its neutral, cationic, and anionic forms were calculated by means of *ab initio* methods. The ground-state equilibrium geometries of the rotamers were determined with the MP2 method.[3] The equilibrium geometries in the lowest excited singlet state have been determined with the CC2 method.[4] To estimate the potential energy barriers separating the minima, the minimum energy profiles were calculated along the relevant driving coordinate – the torsional angle defining rotation of the imidazole unit vs. the phenyl ring, both in the ground S_0 state (MP2) and in the excited singlet state, S_1 (CC2). Dunning's correlation-consistent split-valence double-zeta basis set with polarization functions on all atoms and augmented with the diffuse functions (aug-cc-pVDZ)[5] was employed in all these calculations. For calculations of the UV absorption spectra of different rotameric forms, the vertical excitation energies and response properties in the lowest excited singlet states have been calculated at the CC2/aug-cc-pVDZ theory level[6, 7], using the S_0-state equilibrium rotamer geometry determined at the MP2/aug-cc-pVDZ theory level. All the calculations were performed with the TURBOMOLE program package[8].

Table S1. Vertical excitation energy (ΔE^{VE}, in eV and λ_{abs}, in nm), oscillator strength (f), of the lowest singlet states for the equilibrium forms of the **Neutral-4a** molecule calculated with the **CC2/aug-cc-pVDZ** method at the ground state geometry optimized at the **MP2/aug-cc-pVDZ** theory level. Abbreviations: "dd" = down-down, "uu" – up-up, "r" – rotate, "s" – straight.

S_0 form		ΔE^{VE}	f	λ_{abs}	μ_e
Neutral forms					
4a-dd	S_0	-0.048[a]			μ_g = 3.5
	$S_0 \rightarrow S_1(\pi\pi^*)$	**3.749**	**0.0567**	**331 nm**	3.4
	$S_0 \rightarrow S_2(\pi\pi^*)$	**4.023**	**0.3007**	**308 nm**	2.7
	$S_0 \rightarrow S_3(\pi\pi^*)$	**4.651**	**0.0326**	**267 nm**	3.5
	$S_0 \rightarrow S_4(n\pi^*)$	4.712	0.0010		6.8
	$S_0 \rightarrow S_5(\pi\pi^*)$	**4.852**	**0.6236**	**256 nm**	4.3
	$S_0 \rightarrow S_6(\pi\pi^*)$	**5.020**	**0.5988**	**247 nm**	2.2
	$S_0 \rightarrow S_7(n\pi^*)$	5.052	0.0634		7.0
	$S_0 \rightarrow S_8(n\pi^*)$	5.122	0.0007		2.5
	$S_0 \rightarrow S_9(n\pi^*)$	5.222	0.0070		4.5
	$S_0 \rightarrow S_{10}(n\pi^*)$	5.246	0.0016		4.2
	$S_0 \rightarrow S_{11}(\pi\pi^*)$	**5.392**	**0.0712**	**230 nm**	3.6
	$S_0 \rightarrow S_{12}(n\pi^*)$	5.419	0.0088		4.3
4a-dd-r	S_0	0.00[a]			μ_g = 5.9
	$S_0 \rightarrow S_1(\pi\pi^*)$	**3.950**	**0.0676**	**314 nm**	5.1
	$S_0 \rightarrow S_2(\pi\pi^*)$	**4.155**	**0.0893**	**299 nm**	6.0
	$S_0 \rightarrow S_3(n\pi^*)$	4.559	0.0000		9.2
	$S_0 \rightarrow S_4(\pi\pi^*)$	**4.712**	**0.0433**	**263 nm**	4.8
	$S_0 \rightarrow S_5(n\pi^*)$	4.925	0.0000		11.3
	$S_0 \rightarrow S_6(n\pi^*)$	5.098	0.0081		5.5
	$S_0 \rightarrow S_7(n\pi^*)$	5.129	0.0004		4.3
	$S_0 \rightarrow S_8(n\pi^*)$	5.196	0.0001		16.3
4a-dd-s	S_0	0.036 [a]			μ_g = 6.7
	$S_0 \rightarrow S_1(\pi\pi^*)$	**3.613**	**0.0781**	**343 nm**	3.1
	$S_0 \rightarrow S_2(\pi\pi^*)$	**3.844**	**0.6016**	**323 nm**	4.7
	$S_0 \rightarrow S_3(n\pi^*)$	**4.306**	**0.0645**	**288 nm**	8.3
	$S_0 \rightarrow S_4(n\pi^*)$	4.477	0.0004		9.5
	$S_0 \rightarrow S_5(\pi\pi^*)$	**4.628**	**0.5264**	**268 nm**	3.7
	$S_0 \rightarrow S_6(\pi\pi^*)$	**4.656**	**0.1637**	**267 nm**	4.1
	$S_0 \rightarrow S_7(n\pi^*)$	4.852	0.0014		10.8
	$S_0 \rightarrow S_8(\pi\pi^*)$	**4.867**	**0.2179**	**255 nm**	3.0
4a-uu-r	S_0	0.095 [a]			μ_g = 1.0
	$S_0 \rightarrow S_1(\pi\pi^*)$	3.908	**0.0676**	**318 nm**	1.6
	$S_0 \rightarrow S_2(\pi\pi^*)$	4.139	**0.0964**	**300 nm**	1.6
	$S_0 \rightarrow S_3(n\pi^*)$	4.622	**0.0480**	**268 nm**	1.2
	$S_0 \rightarrow S_4(n\pi^*)$	4.782	0.0001		9.1
	$S_0 \rightarrow S_5(n\pi^*)$	5.080	**0.0324**	**244 nm**	19.3
	$S_0 \rightarrow S_6(n\pi^*)$	5.109	0.0000		5.9
	$S_0 \rightarrow S_7(n\pi^*)$	5.151	0.0029		1.7
	$S_0 \rightarrow S_8(n\pi^*)$	5.285	0.0018		2.4

Anionic - deprotonated forms					
[4a-H]$^-$-uu-r	S_0	0.00 [a]			μ_g = 0.5
	$S_0 \rightarrow S_1(\pi\pi^*)$	**3.239**	**0.0373**	**383 nm**	5.9
	$S_0 \rightarrow S_2(n\pi^*)$	3.269	0.0000		20.9
	$S_0 \rightarrow S_3(n\pi^*)$	3.530	0.0006		14.1
	$S_0 \rightarrow S_4(n\pi^*)$	3.711	0.00002		2.1
	$S_0 \rightarrow S_5(n\pi^*)$	3.873	0.0001		26.8
	$S_0 \rightarrow S_6(\pi\pi^*)$	**3.897**	**0.1370**	**318 nm**	2.7
	$S_0 \rightarrow S_8(n\pi^*)$	3.929	0.0004		10.7
	$S_0 \rightarrow S_9(n\pi^*)$	4.061	0.0067		18.9
	$S_0 \rightarrow S_{10}(n\pi^*)$	4.090	0.0001		16.2
[4a-H]$^-$-dd-r	S_0	0.059 [a]			μ_g = 3.4
	$S_0 \rightarrow S_1(n\pi^*)$	3.228	0.0013		21.4
	$S_0 \rightarrow S_2(\pi\pi^*)$	**3.245**	**0.0350**	**382 nm**	8.6
	$S_0 \rightarrow S_3(n\pi^*)$	3.475	0.0005		14.4
	$S_0 \rightarrow S_4(n\pi^*)$	3.647	0.0004		3.9
	$S_0 \rightarrow S_5(n\pi^*)$	3.772	0.0001		20.7
	$S_0 \rightarrow S_6(n\pi^*)$	3.884	0.0001		10.0
	$S_0 \rightarrow S_6(\pi\pi^*)$	**3.915**	**0.1097**	**317 nm**	4.8
	$S_0 \rightarrow S_6(n\pi^*)$	3.998	0.0029		8.4
	$S_0 \rightarrow S_6(n\pi^*)$	4.050	0.0027		22.0
	$S_0 \rightarrow S_6(n\pi^*)$	4.102	0.0009		4.3
[4a-H]$^-$-ud-r	S_0	0.160 [a]			μ_g = 4.5
	$S_0 \rightarrow S_1(\pi\pi^*)$	3.131	0.0000		24.5
	$S_0 \rightarrow S_2(\pi\pi^*)$	**3.199**	**0.0348**	**388 nm**	9.6
	$S_0 \rightarrow S_3(\pi\pi^*)$	3.382	0.0005		16.3
	$S_0 \rightarrow S_4(\pi\pi^*)$	3.450	0.0004		24.2
	$S_0 \rightarrow S_5(n\pi^*)$	3.607	0.0001		5.4
	$S_0 \rightarrow S_6(\pi\pi^*)$	3.695	0.0001		19.2
	$S_0 \rightarrow S_7(n\pi^*)$	3.891	0.0097		5.5
	$S_0 \rightarrow S_8(n\pi^*)$	**3.896**	**0.1088**	**319 nm**	6.5
	$S_0 \rightarrow S_9(n\pi^*)$	3.921	0.0063		10.2
[4a-H]$^-$-dd-r	S_0	0.380 [a]	**(0.219)**		μ_g = 7.9
	$S_0 \rightarrow S_1(\pi\pi^*)$	2.984	0.0000		28.6
	$S_0 \rightarrow S_2(\pi\pi^*)$	3.123	0.0002		27.0
	$S_0 \rightarrow S_3(\pi\pi^*)$	3.158	**0.0321**	**393 nm**	12.6
	$S_0 \rightarrow S_4(\pi\pi^*)$	3.230	0.0007		20.7
	$S_0 \rightarrow S_5(n\pi^*)$	3.332	0.0002		17.4
	$S_0 \rightarrow S_6(\pi\pi^*)$	3.418	0.0000		1.95
	$S_0 \rightarrow S_7(n\pi^*)$	3.634	0.0000		0.1
	$S_0 \rightarrow S_8(n\pi^*)$	3.718	0.0011		7.2
	$S_0 \rightarrow S_9(n\pi^*)$	3.814	0.0031		29.1
Cationic - protonated forms					
[4a+H]$^+$-dd-s		0.00 [a]			μ_g = 5.8
	$S_0 \rightarrow S_1(\pi\pi^*)$	3.374	**0.0407**	**368 nm**	9.7
	$S_0 \rightarrow S_2(\pi\pi^*)$	3.762		**330 nm**	0.3
	$S_0 \rightarrow S_3(\pi\pi^*)$	3.984		**311 nm**	10.0
	$S_0 \rightarrow S_4(\pi\pi^*)$	4.599		**270 nm**	3.5
	$S_0 \rightarrow S_5(\pi\pi^*)$	4.763		**261 nm**	5.3
	$S_0 \rightarrow S_6(n\pi^*)$	5.268			6.3
	$S_0 \rightarrow S_7(\pi\pi^*)P$	5.296		**234 nm**	3.0
	$S_0 \rightarrow S_8(n\pi^*)P$	5.718			3.2
	$S_0 \rightarrow S_9(n\pi^*)P$	5.741	**0.7478**		3.0

4a+H]$^+$-dd-r		0.324 [a]	**0.0721**		μ_g = 5.3
	$S_0 \rightarrow S_1(\pi\pi^*)$	3.257	**0.6772**	**381 nm**	11.2
	$S_0 \rightarrow S_2(\pi\pi^*)$	3.772	**0.0187**	**329 nm**	2.5
	$S_0 \rightarrow S_3(\pi\pi^*)$	4.224	0.0000	**294 nm**	8.4
	$S_0 \rightarrow S_4(\pi\pi^*)$	4.655	**0.0381**	**267 nm**	1.5
	$S_0 \rightarrow S_5(\pi\pi^*)$	4.688	0.0007		6.0
	$S_0 \rightarrow S_6(\pi\pi^*)$	5.229	**0.0421**		6.0
	$S_0 \rightarrow S_7(n\pi^*)$	5.313	0.0006		7.0
	$S_0 \rightarrow S_8(n\pi^*)$	**5.322**	**0.0645**	**233 nm**	1.3
	$S_0 \rightarrow S_9(n\pi^*)$	5.419	0.0053		6.7
	$S_0 \rightarrow S_{10}(n\pi^*)$	**5.663**	**0.0993**	**219 nm**	20.8
	$S_0 \rightarrow S_{11}(n\pi^*)$	5.726	0.0052		3.2
	$S_0 \rightarrow S_{12}(n\pi^*)$	**5.803**	**0.4425**	**214 nm**	1.1
[4a+H]$^+$-dd-r		0.345 [a]			μ_g = 3.4
	$S_0 \rightarrow S_1(\pi\pi^*)$	**3.664**	**0.0548**	**339 nm**	7.2
	$S_0 \rightarrow S_2(\pi\pi^*)$	**4.104**	**0.1438**	**302 nm**	0.4
	$S_0 \rightarrow S_3(\pi\pi^*)$	**4.563**	**0.0371**	**272 nm**	11.9
	$S_0 \rightarrow S_4(\pi\pi^*)$	**4.592**	**0.0495**	**270 nm**	9.2
	$S_0 \rightarrow S_5(n\pi^*)$	4.877	0.0015		16.6
	$S_0 \rightarrow S_6(n\pi^*)$	4.998	0.0051		7.3
	$S_0 \rightarrow S_7(\pi\pi^*)$	**5.234**	**1.447**	**237 nm**	4.5
	$S_0 \rightarrow S_8(n\pi^*)$	5.371	0.0000		10.2
	$S_0 \rightarrow S_9(\pi\pi^*)$	**5.531**	**0.0432**	**224 nm**	0.5
[4a+H]$^+$-uu-r		1.129 [a]			μ_g = 0.8
	$S_0 \rightarrow S_1(\pi\pi^*)$	3.276	0.0045		9.9
	$S_0 \rightarrow S_2(\pi\pi^*)$	**3.428**	**0.0345**	**362 nm**	8.4
	$S_0 \rightarrow S_3(\pi\pi^*)$	**4.021**	**0.1895**	**309 nm**	5.1
	$S_0 \rightarrow S_4(\pi\pi^*)$	**4.404**	**0.1036**	**282 nm**	2.0
	$S_0 \rightarrow S_5(\pi\pi^*)$	4.430	0.0000		11.4
	$S_0 \rightarrow S_6(\pi\pi^*)$	4.760	0.0113		10.0

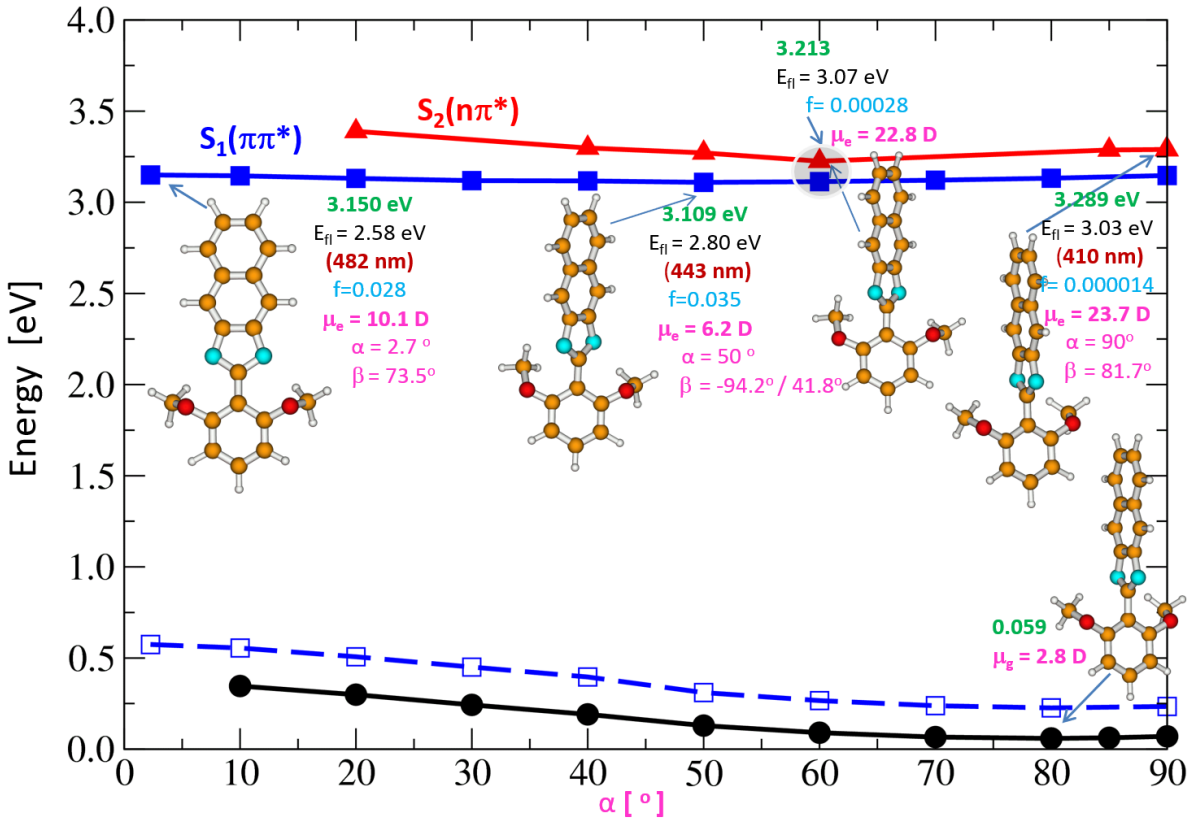


Figure S54. Minimum potential-energy profiles for **[4a-H]**$^-$ for the ground electronic state (S_0) (filled black circles), the lowest emitting excited state $S_1(\pi\pi^*)$ (filled blue squares), and the second lowest dark excited state $S_2(n\pi^*)$ (filled red triangles) as a function of the α (N-C-C-C) dihedral angle optimized with the MP2/aug-cc-pVDZ method, for S_0 state, and with the CC2/aug-cc-pVDZ method, for the excited states, respectively. The α dihedral angle was fixed while the rest of the geometric parameters were being optimized in the calculations of given state. The shaded gray circle shows a conical intersection region between the $S_2(n\pi^*)$ and $S_1(\pi\pi^*)$ excited states. $S_0^{[S1(\pi\pi^*)]}$ denotes the S_0-state energy level calculated at the geometry of the excited state $S_1(\pi\pi^*)$(empty squares, dashed blue curve).

Cartesian coordinates of important structures optimized with the MP2/aug-cc-pVDZ method, for the ground state and with the CC2/aug-cc-pVDZ method, for the excited state.

Neutral forms

Neutral, S_0 –state, E=0.00 eV μ_g =3.5 D

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FINAL HEAT OF FORMATION = -990.857317

C	1.202201	4.752801	0.598460	C	-0.637120	1.134379	-0.609210
C	0.609067	3.507377	0.206039	C	0.601722	1.086160	0.120444
C	-0.648051	3.537640	-0.534333	C	1.226011	2.271229	0.528308
C	-1.232069	4.810057	-0.840588	N	-0.946713	-0.192448	-0.844532
C	-0.625083	5.993546	-0.443721	C	0.044197	-0.965090	-0.260356
C	0.604211	5.964760	0.284194	N	0.997155	-0.234571	0.322998
C	-1.272939	2.330554	-0.946900	C	-0.023847	-2.434995	-0.298583

C	-1.262347	-3.099491	-0.104610	H	-0.278494	-6.350773	-0.490711
C	-1.358809	-4.496825	-0.163229	H	1.927805	-5.197671	-0.869791
C	-0.208827	-5.261064	-0.431102	H	-2.173945	4.833793	-1.399690
C	1.027424	-4.624187	-0.632818	H	-1.088967	6.953475	-0.689968
C	1.123644	-3.222362	-0.571349	H	1.075062	6.902652	0.593319
O	-2.426884	-2.364164	0.114487	H	2.145175	4.728952	1.155381
C	-2.474969	-1.823797	1.455918	H	4.110060	-2.028319	-0.078128
O	2.325693	-2.615554	-0.872488	H	2.714890	-1.883668	1.049654
C	3.191079	-2.509334	0.280806	H	3.421770	-3.512879	0.677002
H	-1.807643	-0.572832	-1.225043	H	-3.407371	-1.248071	1.521130
H	2.170303	2.245871	1.081300	H	-2.484271	-2.646154	2.189352
H	-2.212021	2.358890	-1.508807	H	-1.611847	-1.164535	1.646256
H	-2.335252	-4.963350	-0.009094				

Neutral, S_1 ($\pi\pi^*$) state, E=3.397 eV μ_g = 7.5 D

39

FINAL HEAT OF FORMATION = -990.777531

C	1.420870	4.829006	0.037525	O	-2.408901	-2.343122	-0.100879
C	0.759734	3.590513	-0.089664	C	-2.593868	-2.159801	1.326760
C	-0.673483	3.605175	-0.342628	O	2.486652	-2.693189	-0.475965
C	-1.349142	4.837582	-0.451296	C	2.975653	-2.453393	0.862884
C	-0.659967	6.075754	-0.318233	H	-1.936463	-0.553627	-0.599797
C	0.718640	6.064082	-0.075531	H	2.558296	2.355313	0.210129
C	-1.375420	2.354951	-0.474406	H	-2.457341	2.352110	-0.656998
C	-0.642955	1.162086	-0.361341	H	-2.343633	-4.886341	-0.574230
C	0.792578	1.118252	-0.106784	H	-0.272739	-6.312639	-0.946852
C	1.477362	2.343879	0.025650	H	2.005937	-5.199059	-0.820793
N	-1.010418	-0.140587	-0.443643	H	-2.429165	4.833579	-0.643058
C	0.145477	-0.975307	-0.243879	H	-1.205426	7.019735	-0.406066
N	1.252831	-0.155613	-0.029961	H	1.269479	7.004335	0.029807
C	0.053949	-2.391175	-0.320061	H	2.500641	4.836702	0.227916
C	-1.220666	-3.074864	-0.339270	H	3.929687	-1.921025	0.747688
C	-1.340034	-4.448325	-0.564296	H	2.270636	-1.822084	1.425849
C	-0.185709	-5.238250	-0.759771	H	3.132851	-3.417356	1.378728
C	1.085868	-4.620606	-0.687024	H	-3.513403	-1.568577	1.449957
C	1.214566	-3.245245	-0.466183	H	-2.702049	-3.140690	1.816935
				H	-1.730925	-1.622181	1.758783

Cationic forms

Cation, S_0 – state, E=0.324 eV μ_e =5.3 D

40

FINAL HEAT OF FORMATION = -991.249233

C	1.417467	4.894041	-0.103589	C	0.711568	1.237430	-0.068038
C	0.728412	3.638583	-0.090695	C	1.453681	2.417839	-0.078022
C	-0.732532	3.638735	-0.091783	N	-1.097304	-0.103759	-0.058251
C	-1.421306	4.894335	-0.105806	C	-0.002569	-0.900391	-0.056452
C	-0.716288	6.088338	-0.117706	N	1.092323	-0.103977	-0.056444
C	0.712716	6.088189	-0.116608	C	-0.002679	-2.359115	-0.112408
C	-1.458095	2.418155	-0.080197	C	-1.223019	-3.083691	-0.188829
C	-0.716265	1.237578	-0.069137	C	-1.221218	-4.471277	-0.382782

C	-0.002718	-5.163921	-0.487910	H	2.172763	-4.994323	-0.457844
C	1.215786	-4.471509	-0.381286	H	-2.515748	4.896128	-0.107554
C	1.217618	-3.083936	-0.187248	H	-1.256747	7.038770	-0.128628
O	-2.434931	-2.408165	-0.072489	H	1.253389	7.038508	-0.126778
C	-2.986732	-2.537528	1.271307	H	2.511912	4.895610	-0.103561
O	2.429518	-2.408687	-0.069142	H	3.938853	-2.006275	1.262613
C	2.979419	-2.538375	1.275405	H	2.291906	-2.086356	2.009709
H	-2.028510	-0.520494	-0.129681	H	3.140313	-3.598822	1.517174
H	2.547443	2.418180	-0.079441	H	-3.945982	-2.005133	1.257118
H	-2.551855	2.418742	-0.083125	H	-3.148269	-3.597898	1.512987
H	-2.178206	-4.993907	-0.460453	H	-2.300098	-2.085632	2.006510
H	-0.002717	-6.243929	-0.655324	H	2.023555	-0.520903	-0.126395

Cation, $S_1(\pi\pi^*)$, E=3.243 eV μ_g = 10.1 D

40

FINAL HEAT OF FORMATION = -991.187856

C	1.176917	-3.144888	0.239589	C	-2.988761	-2.593183	-1.311908
C	-0.032729	-2.373031	0.119153	O	2.407422	-2.484938	0.078144
C	-1.272995	-3.097831	0.218502	C	2.936877	-2.706872	-1.260850
C	-1.298487	-4.467193	0.493996	H	-2.055233	-0.458772	0.049364
C	-0.091311	-5.184255	0.654324	H	2.600984	2.359144	0.057147
C	1.145089	-4.514118	0.515063	H	-2.482088	2.456257	0.011911
C	-0.004557	-0.977643	-0.044731	H	-2.268073	-4.966577	0.588341
N	-1.111437	-0.080100	-0.068967	H	-0.113837	-6.252317	0.887557
C	-0.684279	1.216755	-0.018764	H	2.093015	-5.050302	0.626076
C	0.757988	1.189178	-0.006071	H	-2.395586	4.932129	0.083291
N	1.136066	-0.123066	-0.048970	H	-1.108762	7.081250	0.160847
C	1.505327	2.377346	0.038794	H	1.402838	7.033257	0.183261
C	0.805463	3.628885	0.069012	H	2.607823	4.836552	0.128080
C	-0.639880	3.656516	0.056086	H	3.902297	-2.183407	-1.299629
C	-1.386382	2.432601	0.013106	H	3.083812	-3.783196	-1.436385
C	-1.299462	4.905929	0.090732	H	2.240882	-2.297535	-2.014002
C	-0.568320	6.130560	0.135496	H	-3.932586	-2.033087	-1.367121
C	0.827013	6.103896	0.147962	H	-2.264774	-2.211013	-2.052848
C	1.511541	4.852221	0.115893	H	-3.173772	-3.663152	-1.490227
O	-2.474303	-2.391236	0.036084	H	2.062556	-0.537496	0.085208

Anionic forms

Anion, S_0 –state, E=0.059 eV μ_g = 3.4 D

38

FINAL HEAT OF FORMATION = -990.324396

C	3.234537	-0.172317	-1.236092	C	-0.971053	-0.875323	-0.269330
C	2.523019	-0.262454	-0.010979	N	0.327622	-1.319826	-0.399177
C	3.277777	-0.463182	1.172082	C	-2.156698	1.183215	0.481302
C	4.676171	-0.594582	1.151786	C	-3.385094	0.544860	0.180449
C	5.356651	-0.529328	-0.078186	C	-3.399811	-0.822441	-0.349468
C	4.639361	-0.309189	-1.263908	C	-2.185746	-1.519448	-0.567525
C	1.038260	-0.241543	0.044772	C	-4.671027	-1.423801	-0.637089
N	0.351709	0.869731	0.453027	C	-5.866722	-0.747119	-0.427155
C	-0.956583	0.483251	0.257552	C	-5.852356	0.587642	0.089918

C	-4.642701	1.206576	0.382242	H	-4.681311	-2.446920	-1.033110
O	2.626357	-0.616218	2.390560	H	-6.820498	-1.234686	-0.656825
C	2.298794	0.658319	2.984164	H	-6.795135	1.120480	0.255633
O	2.653811	0.001017	-2.473896	H	-4.631380	2.229516	0.778961
C	1.450060	0.798601	-2.551425	H	1.764703	0.427509	3.917018
H	-2.151903	2.205245	0.879588	H	3.226101	1.215750	3.213087
H	-2.201411	-2.543475	-0.959632	H	1.650319	1.237844	2.308629
H	5.143936	-0.241823	-2.231945	H	1.411791	1.143065	-3.595407
H	6.445439	-0.638644	-0.112192	H	0.557814	0.201893	-2.314037
H	5.204052	-0.770107	2.093565	H	1.511147	1.657913	-1.866957

Anion, $S_1(\pi\pi^*)$ state, E=3.109 eV μ_e = 6.2 D

38

FINAL HEAT OF FORMATION = -990.259825

C	3.231249	-0.133100	-1.284445	O	2.587079	-0.732832	2.326585
C	2.493219	-0.281842	-0.065911	C	2.466591	0.495454	3.078424
C	3.252666	-0.531200	1.119504	O	2.645472	0.198551	-2.493152
C	4.646672	-0.698576	1.088937	C	1.623961	1.226799	-2.447883
C	5.337128	-0.614822	-0.139472	H	-2.228089	1.319448	1.945296
C	4.627536	-0.316388	-1.319021	H	-2.234037	-1.744041	-2.110342
C	1.035612	-0.271903	-0.039505	H	5.138571	-0.195398	-2.279459
N	0.287937	0.448009	0.884757	H	6.422348	-0.758511	-0.174025
C	-1.026658	0.200526	0.504614	H	5.166775	-0.931033	2.024021
C	-1.028567	-0.661510	-0.645894	H	-4.737395	-1.682777	-2.116102
N	0.283780	-0.964323	-0.991561	H	-6.920345	-0.869390	-1.149777
C	-2.229573	0.660612	1.066908	H	-6.916291	0.655976	0.842032
C	-3.486019	0.261306	0.478099	H	-4.728611	1.374122	1.872016
C	-3.488448	-0.627677	-0.683224	H	1.904421	0.238918	3.988178
C	-2.234282	-1.082469	-1.234124	H	3.470168	0.874635	3.346955
C	-4.737511	-1.013587	-1.245553	H	1.905246	1.239958	2.492853
C	-5.972903	-0.553056	-0.696803	H	1.757345	1.812039	-3.370623
C	-5.970714	0.299168	0.416039	H	0.619986	0.777813	-2.421251
C	-4.732449	0.707479	0.999427	H	1.768130	1.873623	-1.566516

Anion, $S_1(n\pi^*)$ state, E=3.213 eV μ_e = 22.8 D

38

FINAL HEAT OF FORMATION = -990.255996

C	3.255644	0.090821	-1.277038	C	-3.426734	-0.758833	-0.536919
C	2.518365	-0.202564	-0.099862	C	-2.178446	-1.349583	-0.953260
C	3.227525	-0.627023	1.052998	C	-4.666182	-1.295768	-0.966958
C	4.623341	-0.782289	1.045564	C	-5.882148	-0.707014	-0.574835
C	5.332223	-0.517221	-0.144497	C	-5.883394	0.423441	0.268847
C	4.658593	-0.074118	-1.294760	C	-4.668051	0.968209	0.720696
C	1.041878	-0.202856	-0.061838	O	2.504111	-0.972515	2.188617
N	0.321816	0.737048	0.638000	C	2.342267	0.160842	3.079061
C	-0.990438	0.385013	0.360378	O	2.699327	0.521564	-2.461572
C	-0.987922	-0.775716	-0.508037	C	1.512212	1.351851	-2.382540
N	0.324619	-1.140911	-0.767167	H	-2.192549	1.850196	1.440726
C	-2.182927	0.973813	0.780379	H	-2.180672	-2.233391	-1.603562
C	-3.428515	0.403941	0.328659	H	5.194417	0.154421	-2.220291

H	6.419126	-0.645975	-0.171856
H	5.128467	-1.132525	1.950342
H	-4.668201	-2.175487	-1.622358
H	-6.832259	-1.126463	-0.924597
H	-6.833192	0.877548	0.573049
H	-4.672738	1.848155	1.375906

H	1.751863	-0.208127	3.929009
H	3.330318	0.512294	3.426603
H	1.801555	0.970568	2.562732
H	1.529760	1.957233	-3.299453
H	0.598982	0.738306	-2.355160
H	1.557957	2.003115	-1.495005

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