Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supporting information

Tuning linear dichroism/birefringence (LDLB) contributions in VCD spectra of tartaric acid-$TPPS_4$ porphyrin films

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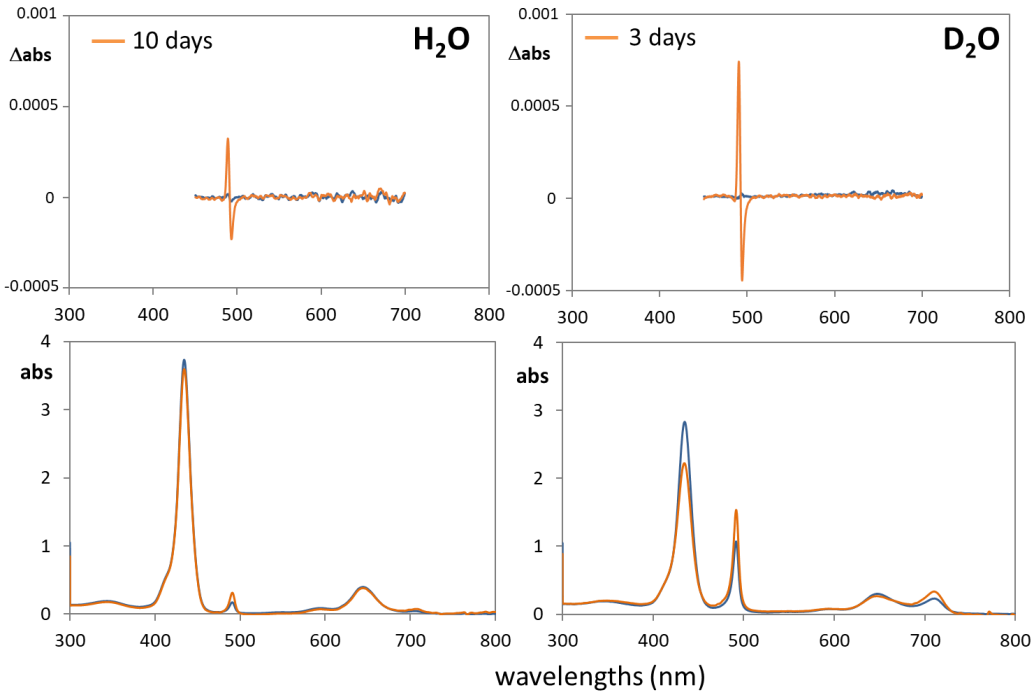


Figure S1. ECD (upper panels) and UV (lower panels) spectra in H_2O (left) and D_2O (right) solutions of 1 mM solutions of $TPPS_4$. Blue lines refer to fresh recorded solutions. Orange lines refer to ECD-UV spectra of H_2O and D_2O recorded after ten and three days respectively. (0.1 mm quartz cuvette employed).

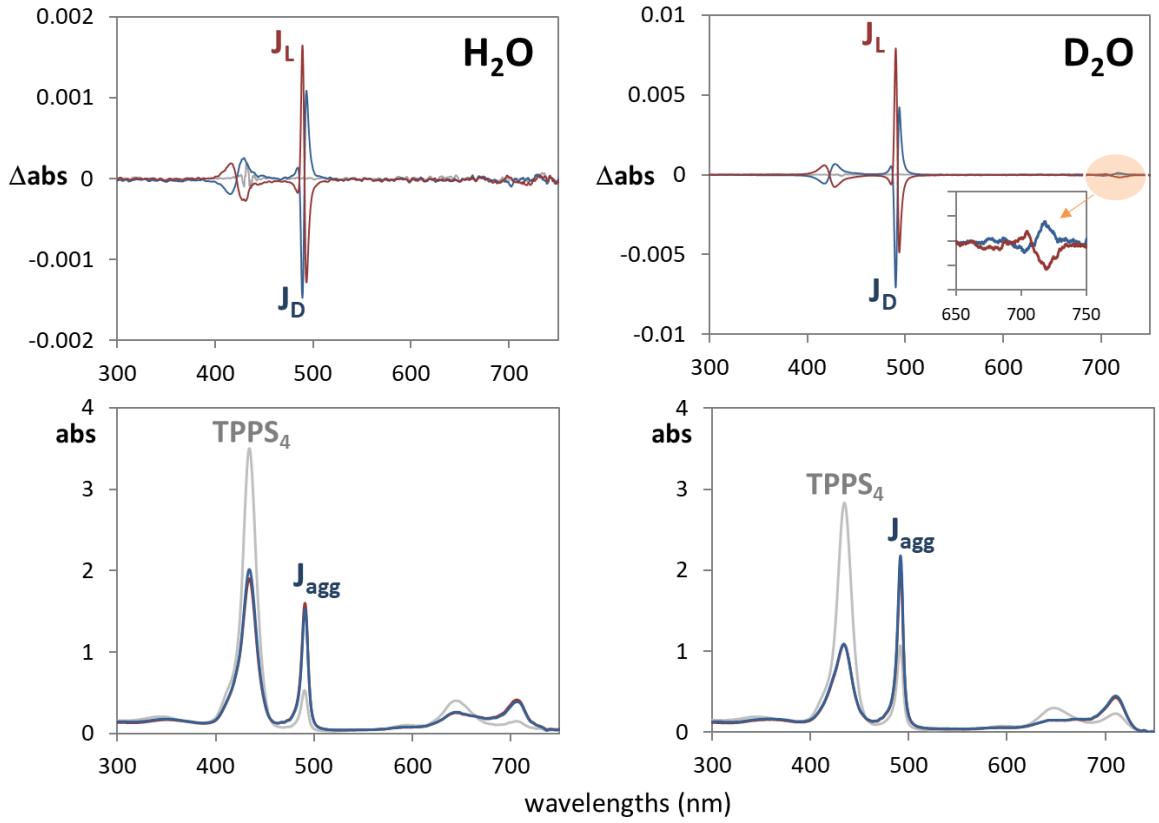


Figure S2. ECD (upper panels) and UV (lower panels) spectra in solution of H_2O (left) and D_2O (right) of J-aggregates J_D (blue lines) and J_L (red lines). Grey lines refer to 1 mM $TPPS_4$ solution. In upper-right panel inset we repeat the magnified portion of the spectra in the 750-650 nm Q bands range. Experimental conditions: [$TPPS_4$] = 0.6 mM; [TA] = 40 mM. Molar ratio [TA/$TPPS_4$] ≈ 67. (0.1 mm quartz cuvette employed).

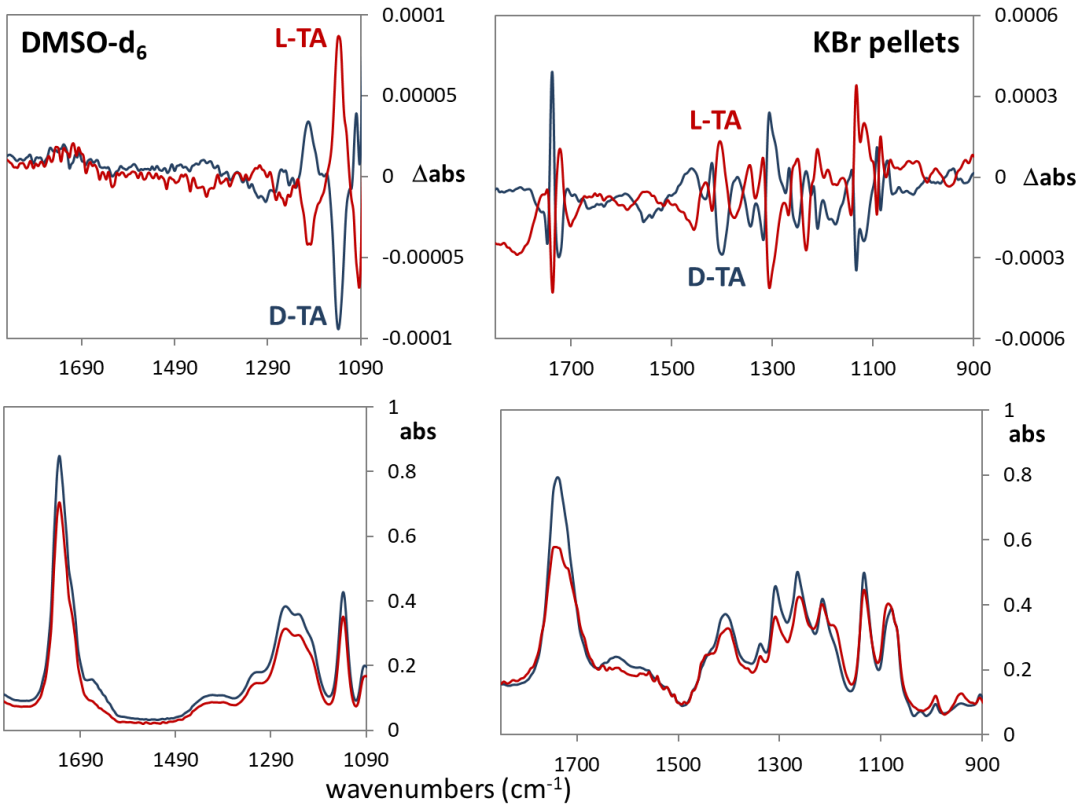


Figure S3. VCD and IR spectra of D/L-TA in DMSO-d_6 solution (left panels) and as KBr pellets (right panels). For the experimental conditions see text.

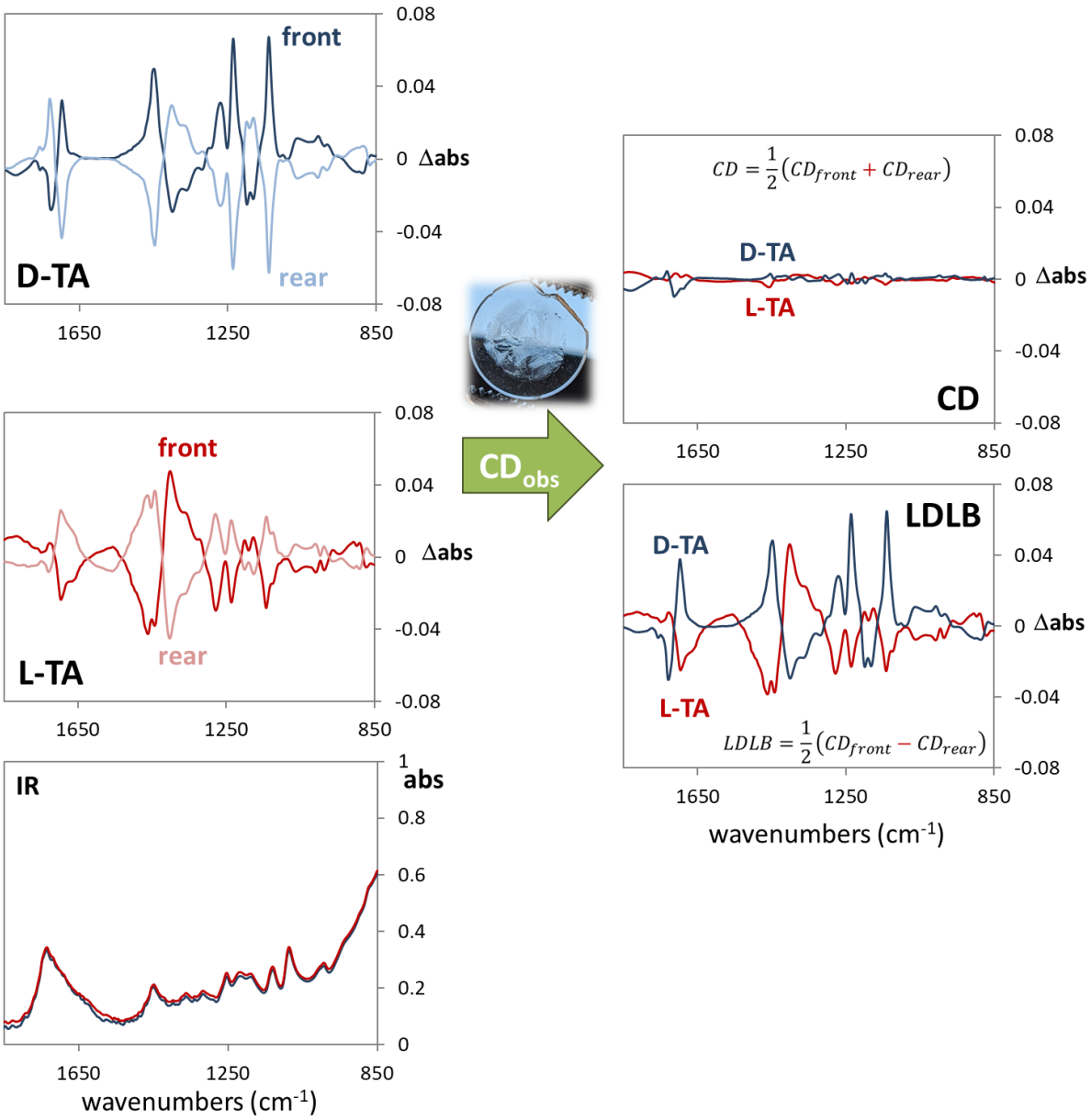


Figure S4. Left panels: Film VCD and IR spectra of mere TA. Comparison between front/rear (dark/light color traces) position of films of D-TA (blue lines) and L-TA (red lines). Right panels: Derived D-TA (blue lines) and L-TA (red lines) true CD (CD, upper panels) and anisotropic contribution (LDLB, lower panels) obtained as reported in equations (2) in the text.

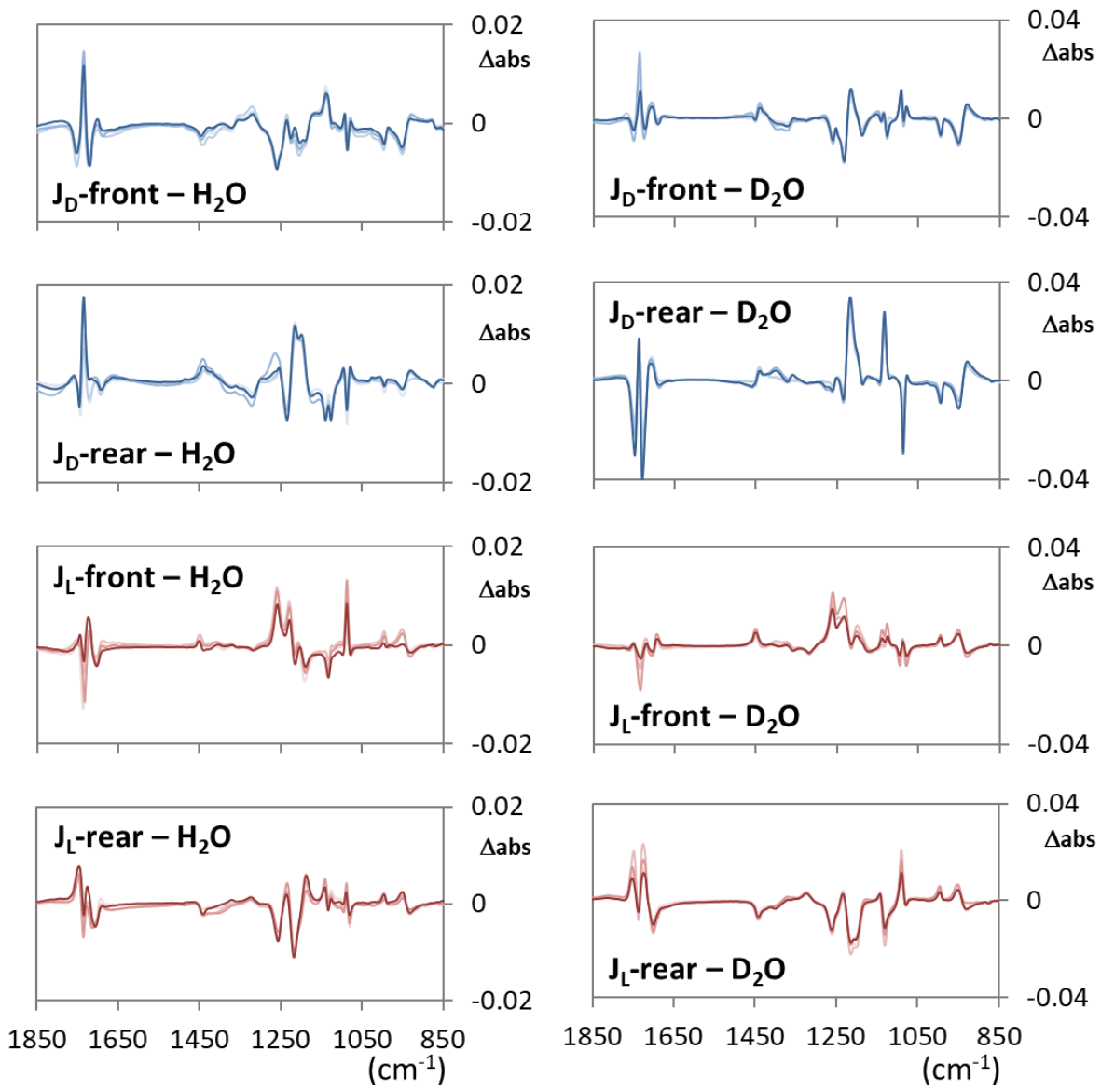


Figure S5. VCD spectra of solid film of J_D (blue lines) and J_L (red lines) rotating sample in four 90° steps, and in "front" and "rear" setup. Depicted VCD spectra refer to H_2O (left panels) and D_2O (right panels) drop cast solutions on CaF_2 plates. Experimental conditions: [$TPPS_4$] = 0.6 mM; [TA] = 40 mM. Molar ratio [TA/$TPPS_4$] ≈ 67.

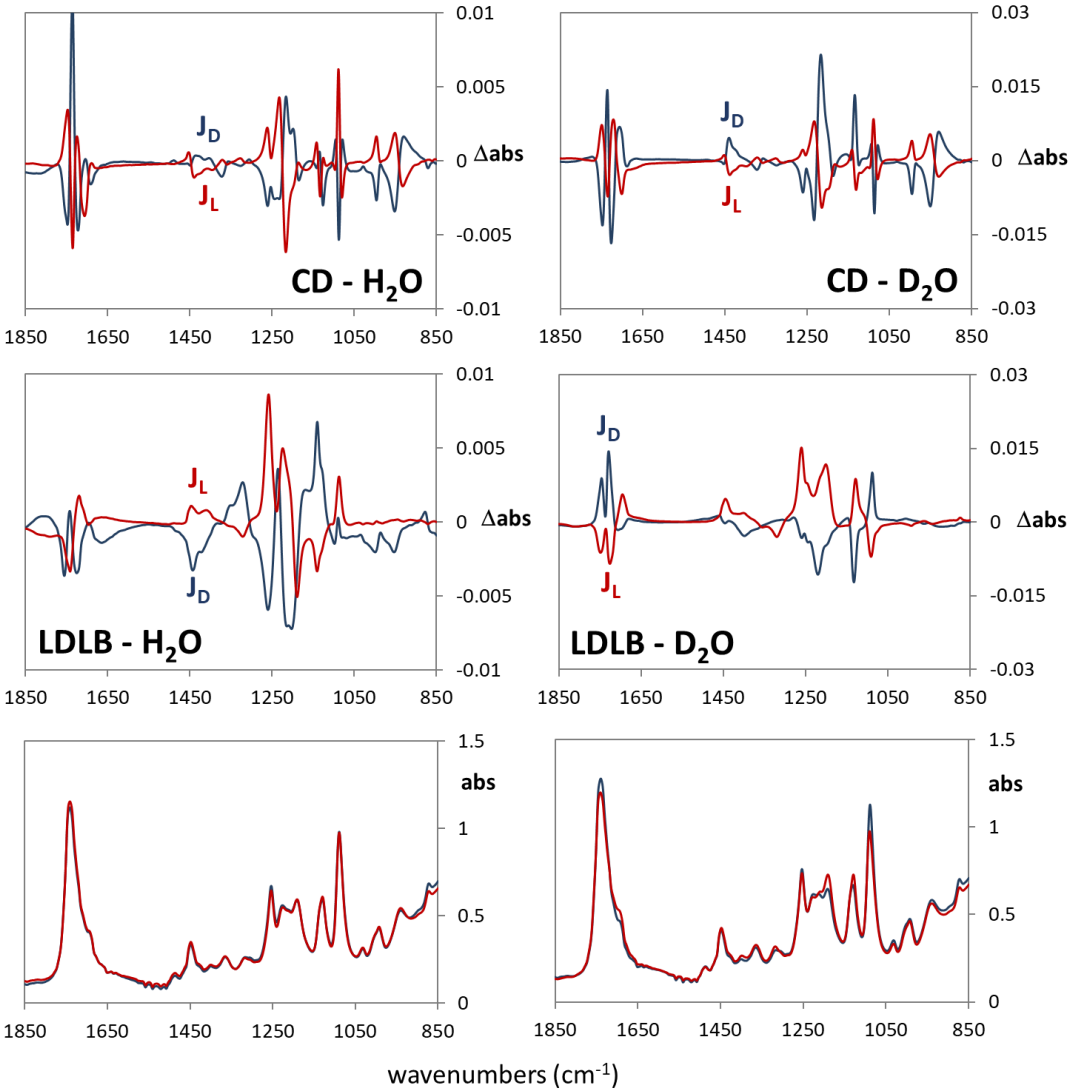


Figure S6. Comparison of J_D (blue lines) and J_L (red lines) CD (top panels), LDLB (middle panels) and IR spectra (lower panels) aggregates in drop cast films. H_2O (left panels) and D_2O (right panels). Experimental conditions: [$TPPS_4$] = 0.6 mM; [TA] = 40 mM. Molar ratio [TA/$TPPS_4$] ≈ 67

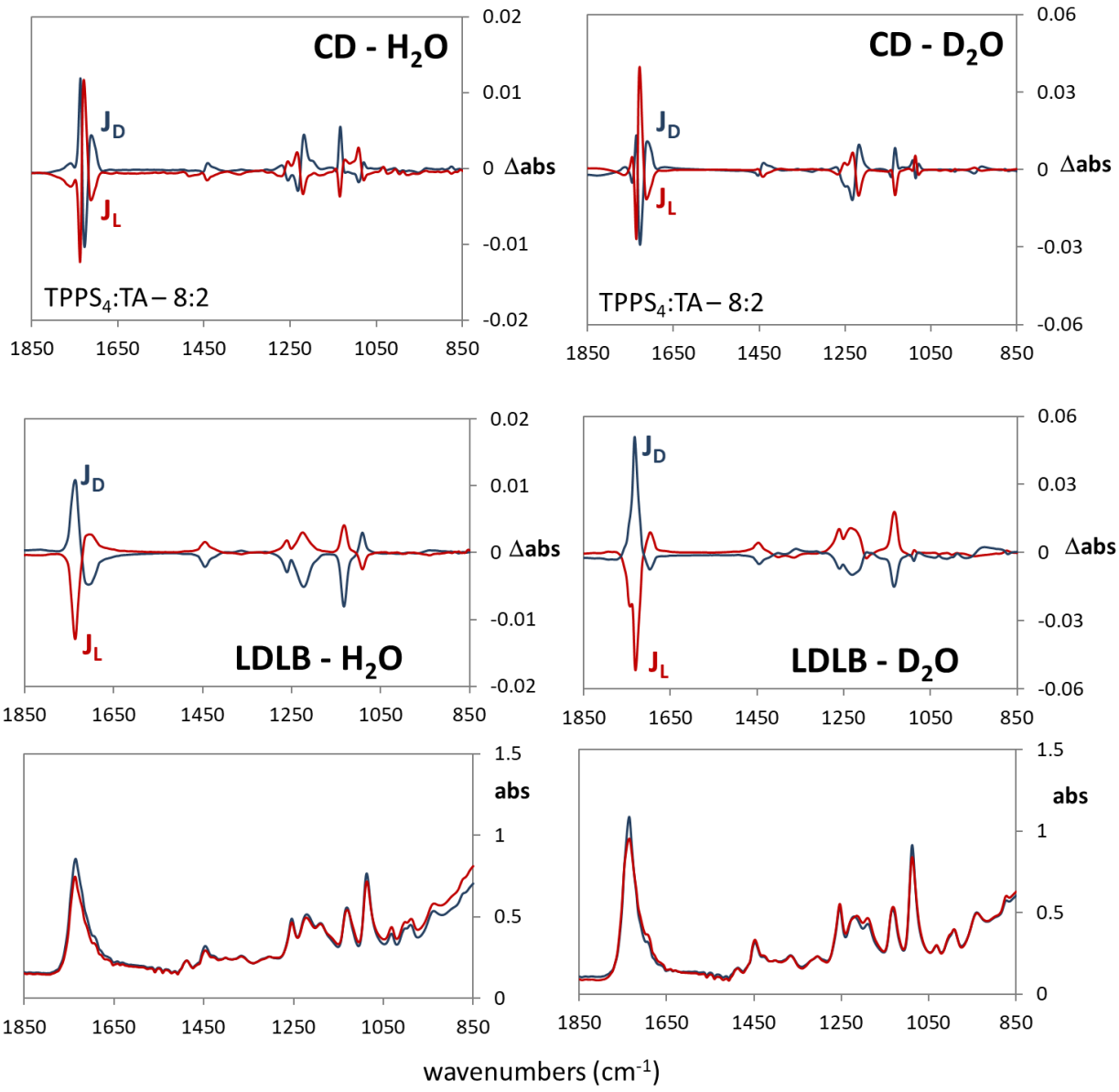


Figure S7 Comparison of J_D (blue lines) and J_L (red lines) CD (top panels), LDLB (middle panels) and IR spectra (lower panels). . Experimental conditions: [$TPPS_4$] = 0.8 mM; [TA] = 20 mM (lower panel). Molar ratio [TA/$TPPS_4$] ≈ 25. Depicted VCD spectra refer to H_2O (left panels) and D_2O (right panels) drop cast solutions on CaF_2 plates.

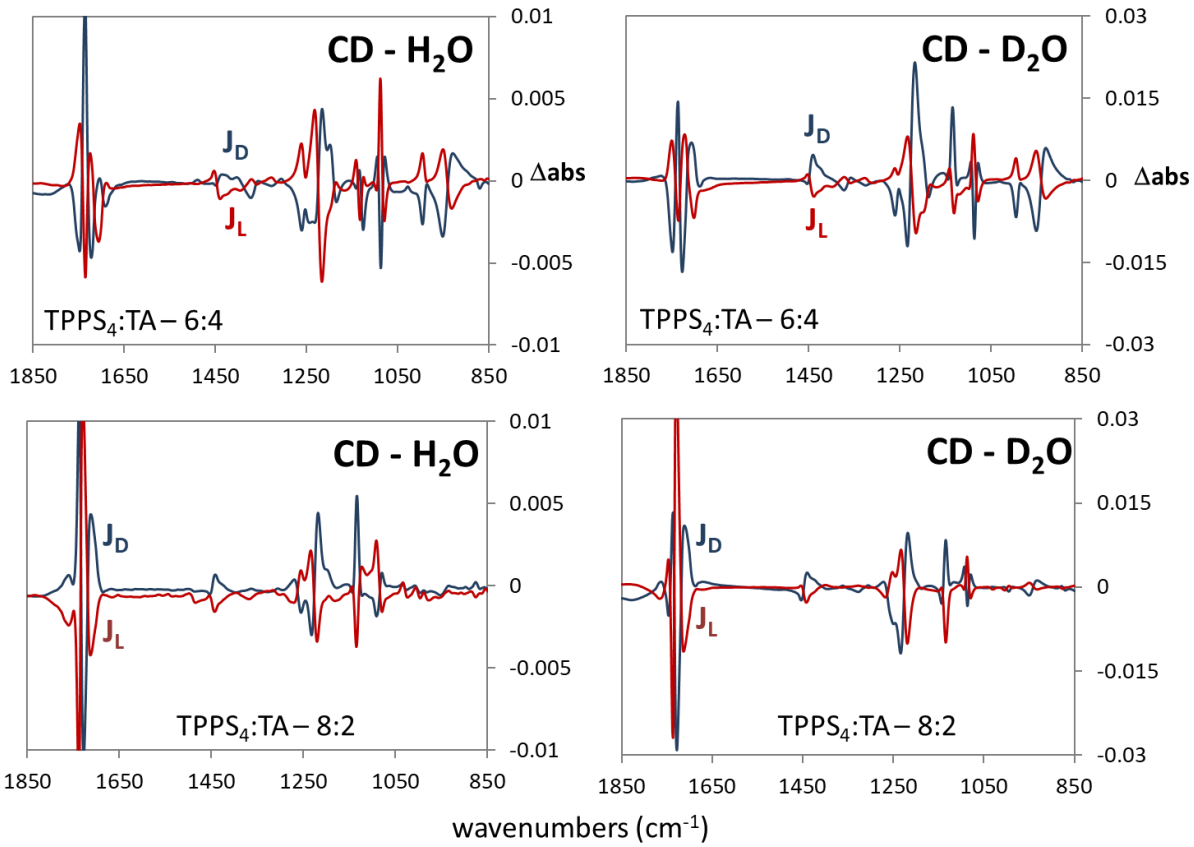
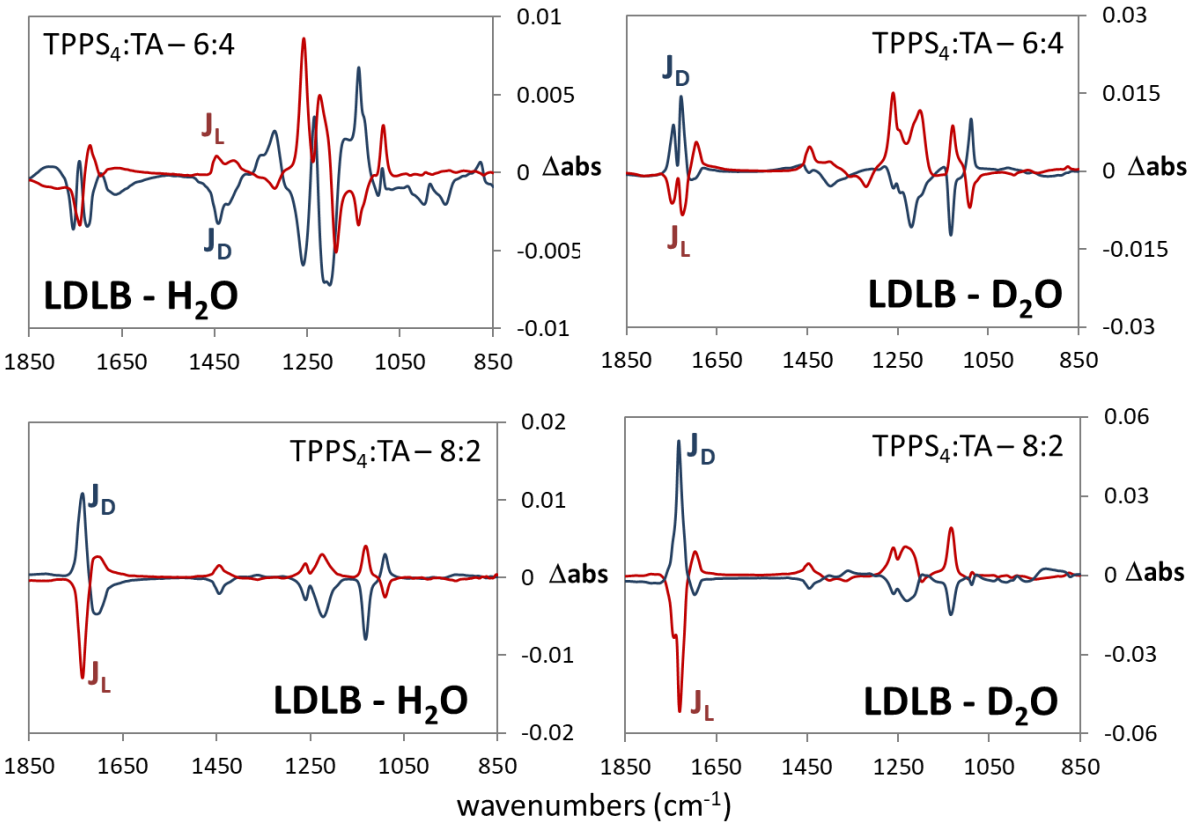


Figure S8 850-1850 cm^{-1} range. Comparison of J_D (blue lines) and J_L (red lines) VCD spectra "true" CD obtained as reported in equations (2). Upper panels experimental conditions: [$TPPS_4$] = 0.6 mM; [TA] = 40 mM (lower panel). Molar ratio [TA/$TPPS_4$] ≈ 67. Lower panels experimental conditions: [$TPPS_4$] = 0.8 mM; [TA] = 20 mM (lower panel). Molar ratio [TA/$TPPS_4$] ≈ 25. Depicted VCD spectra refer to H_2O (left panels) and D_2O (right panels) drop cast solutions on CaF_2 plates.



. **Figure S9** 850-1850 cm^{-1} range. Comparison of J_D (blue lines) and J_L (red lines) VCD LDLB spectra, obtained as reported in equations (2). Upper panels experimental conditions: [$TPPS_4$] = 0.6 mM; [TA] = 40 mM (lower panel). Molar ratio [TA/$TPPS_4$] ≈ 67. Lower panels experimental conditions: [$TPPS_4$] = 0.8 mM; [TA] = 20 mM (lower panel). Molar ratio [TA/$TPPS_4$] ≈ 25. Depicted VCD spectra refer to H_2O (left panels) and D_2O (right panels) drop cast solutions on CaF_2 plates.

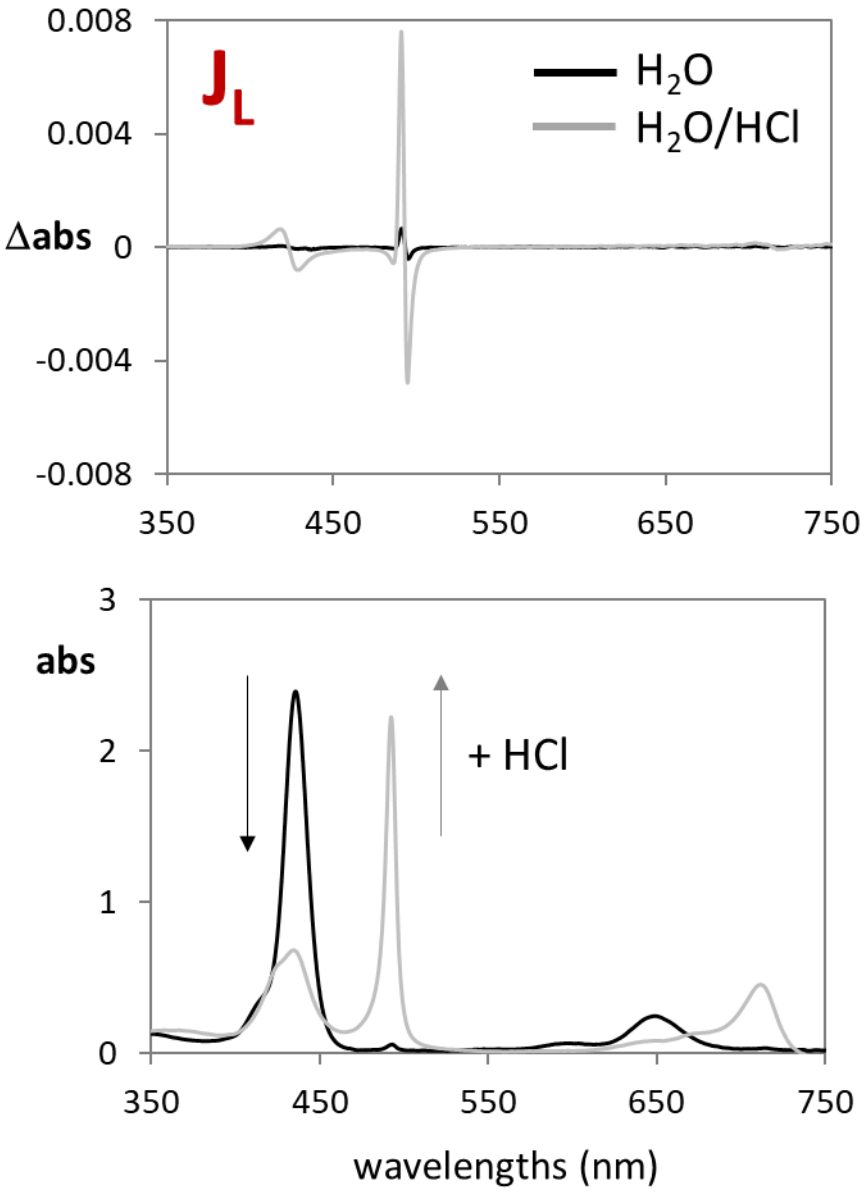


Figure S10. ECD (upper panel) and UV (lower panel) comparison spectra in solution of H_2O (black lines) and acidified H_2O (gray lines) of J-aggregate J_L solutions. (0.1 mm quartz cuvette; for the rest of experimental conditions see text)

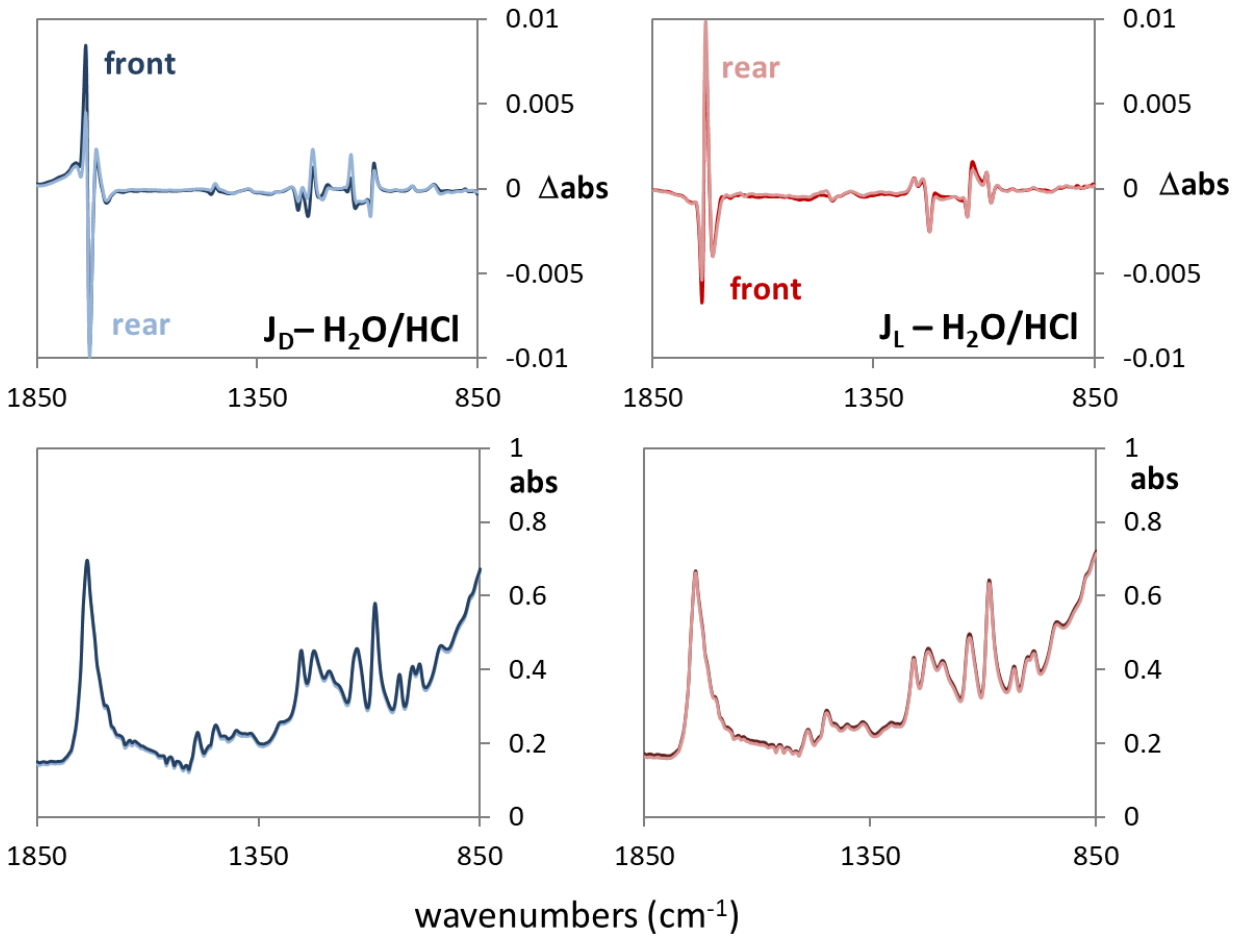


Figure S11. VCD (upper panels) and IR (lower panels) spectra comparison between front/rear (dark/light color traces) position of films of J_D (left) and J_L (right). Experimental conditions: drop cast film from H_2O/HCl solution on CaF_2 plates: [$TPPS_4$] = 0.77 mM; [TA] = 19.2 mM; [HCl] = 38.5 mM.

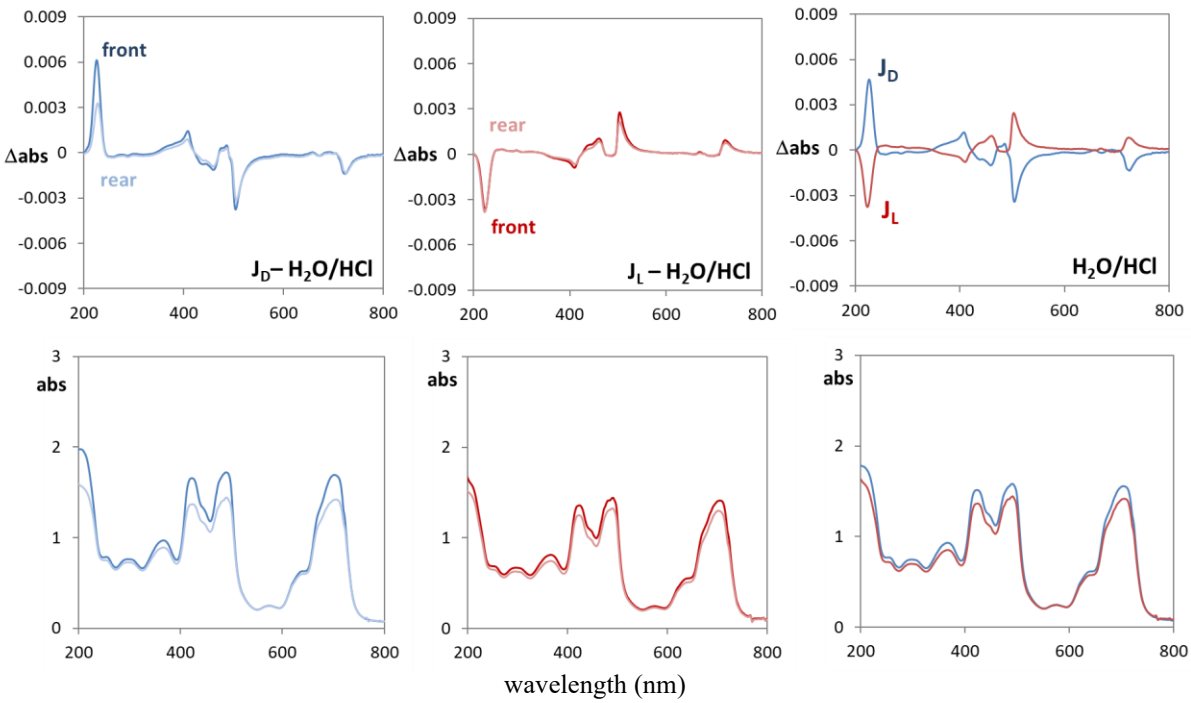


Figure S12. ECD (upper panels) and UV (lower panels) spectra comparison between front/rear (dark/light color traces) position of films of J_D (left) J_L (middle) and superposition of the average spectra for the two enantiomeric systems (right); Experimental conditions: drop cast film from H_2O/HCl solution on CaF_2 plates: [$TPPS_4$] = 0.77 mM; [TA] = 19.2 mM; [HCl] = 38.5 mM.

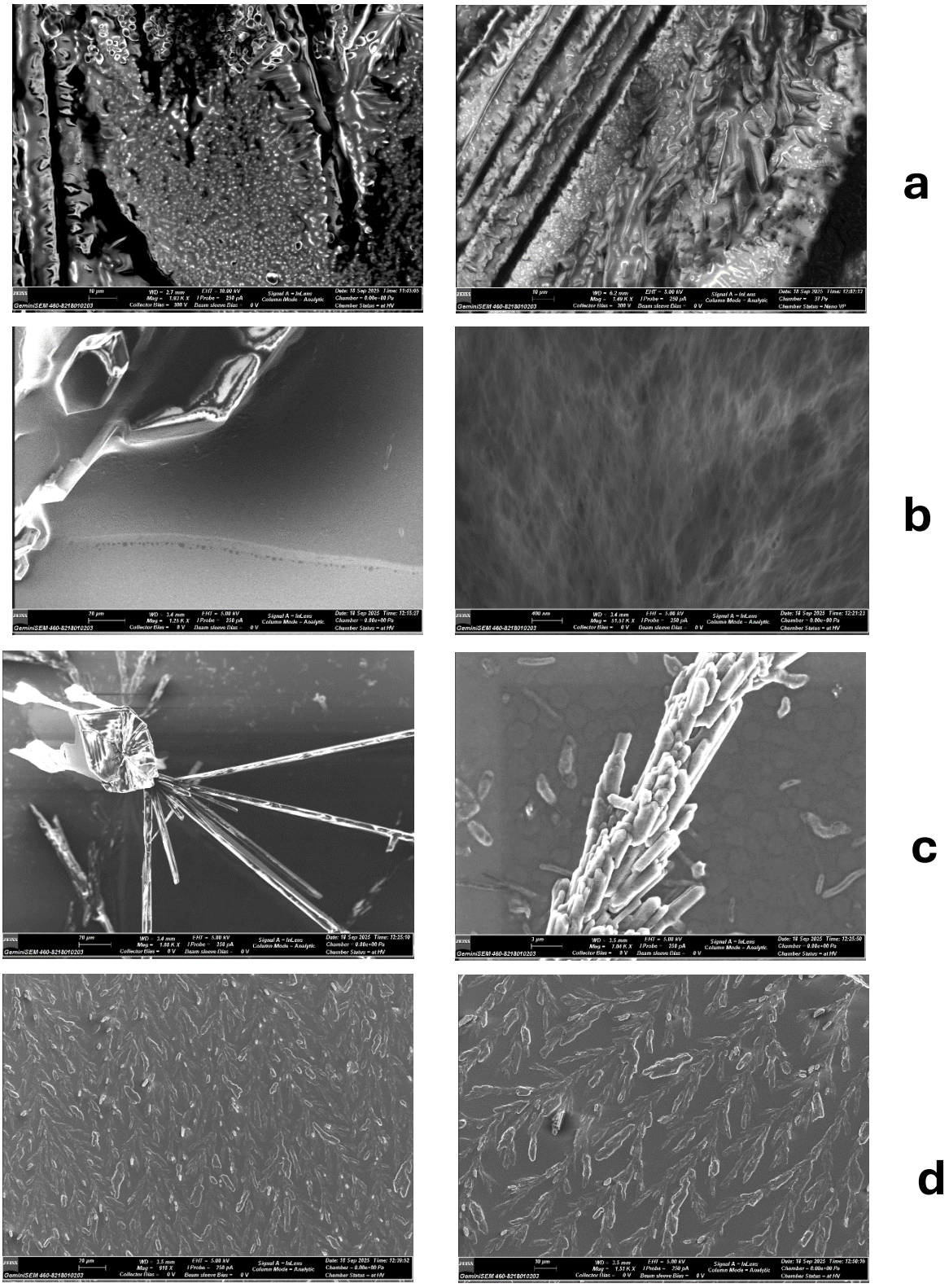


Figure S13. SEM images of a) TA, b) TA/J-aggregated $TPPS_4$ at $[TA/TPPS_4] \approx 67$, c) TA/J-aggregated $TPPS_4$ at $[TA/TPPS_4] \approx 25$, and d) TA/J-aggregated $TPPS_4$ at $[TA/TPPS_4] \approx 67$ after treatment with HCl. With the exclusion of the TA samples, right panels report higher magnification images. The samples were obtained by drop cast solutions of the samples used for the spectroscopic measurements directly onto Si wafer.

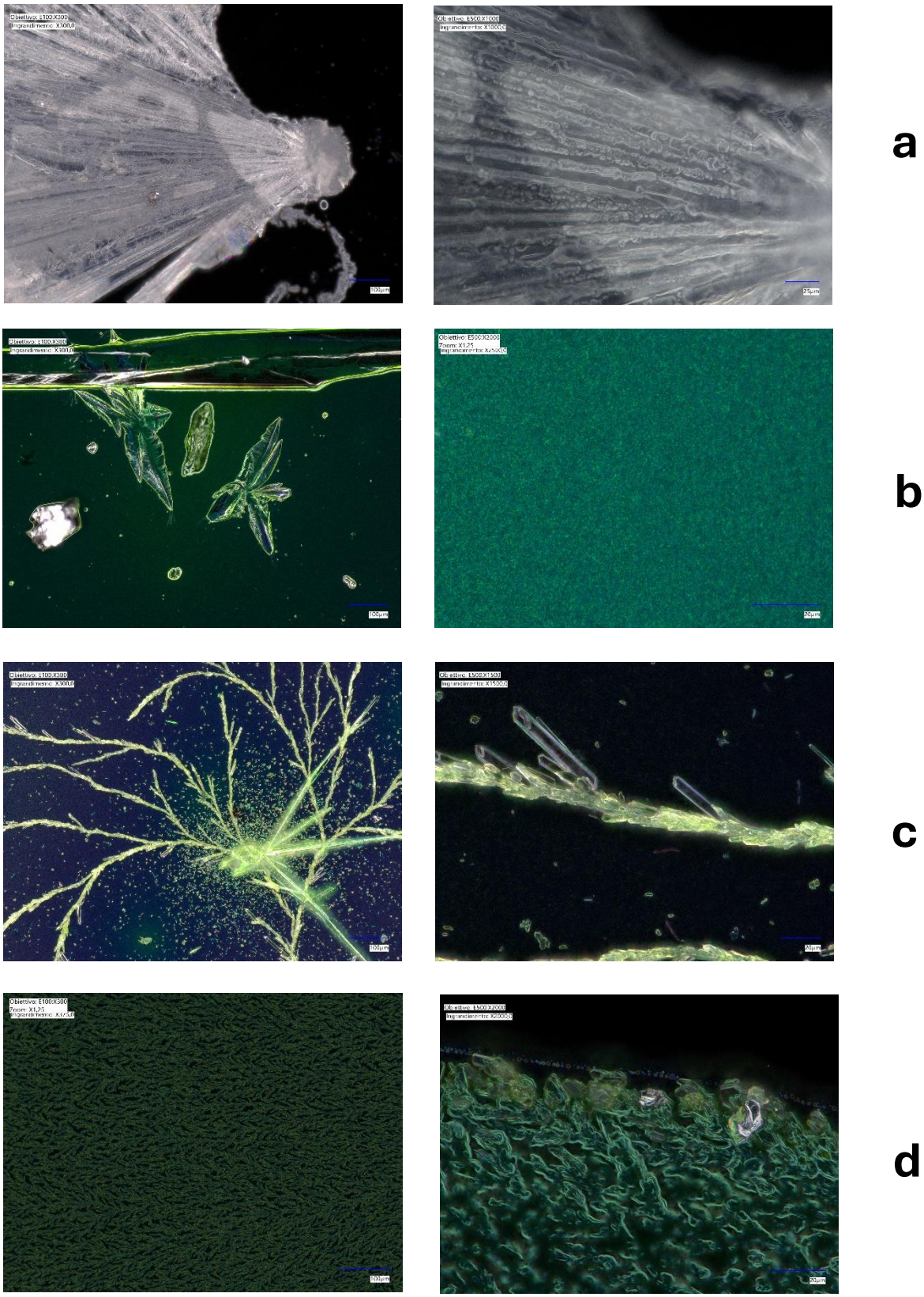


Figure S14. Dark field optical images of a) TA, b) TA/J-aggregated $TPPS_4$ at [TA/$TPPS_4$] ≈ 67, c) TA/J-aggregated $TPPS_4$ at [TA/$TPPS_4$] ≈ 25, and d) TA/J-aggregated $TPPS_4$ at [TA/$TPPS_4$] ≈ 67 after treatment with HCl. Right panels report higher magnification images. The samples were obtained by drop cast solutions of the samples used for the spectroscopic measurements directly onto Si wafer.