Supporting information for

Using Excimeric Fluorescence to Study How the Cooling Rate Determines the Behavior of Naphthalenes in Freeze-Concentrated Solutions: Vitrification and Crystallization

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Number of pages: 24

Number of figures: 14

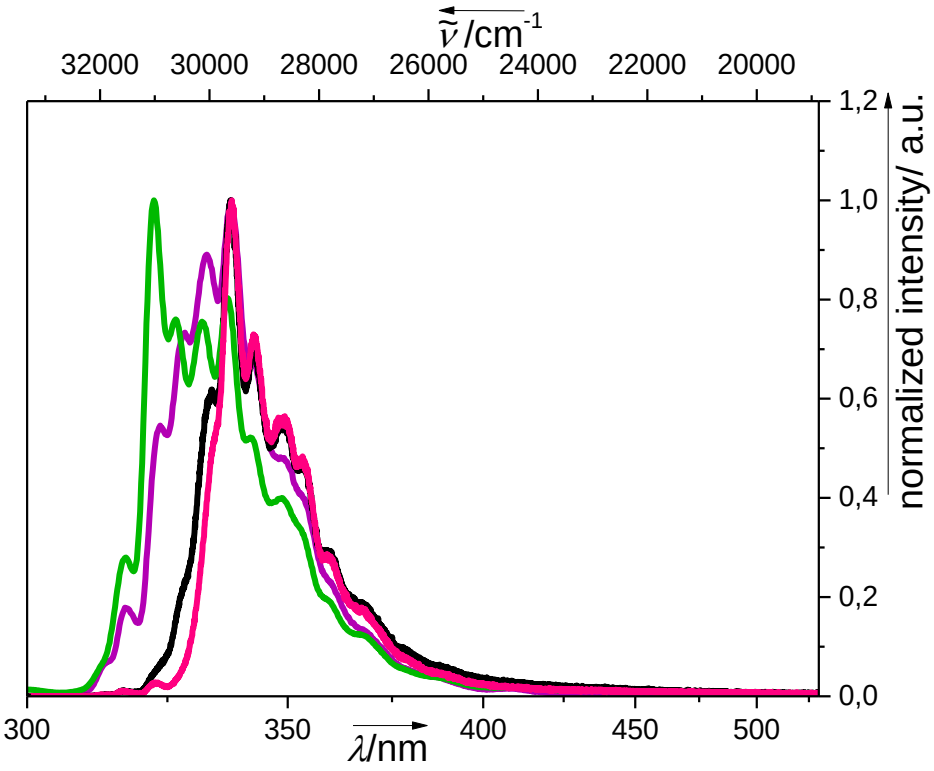

Figure S1. The normalized fluorescence emission spectra (λ_{exc}= 274 nm) of naphthalene: the vapor deposited sample at 253 K on ice spheres (green) forming thin crystals,[1] microcrystals in a thin film on glass (298 K, purple), powdered naphthalene crystals (253 K, black), and macroscopic crystals (253 K, pink).

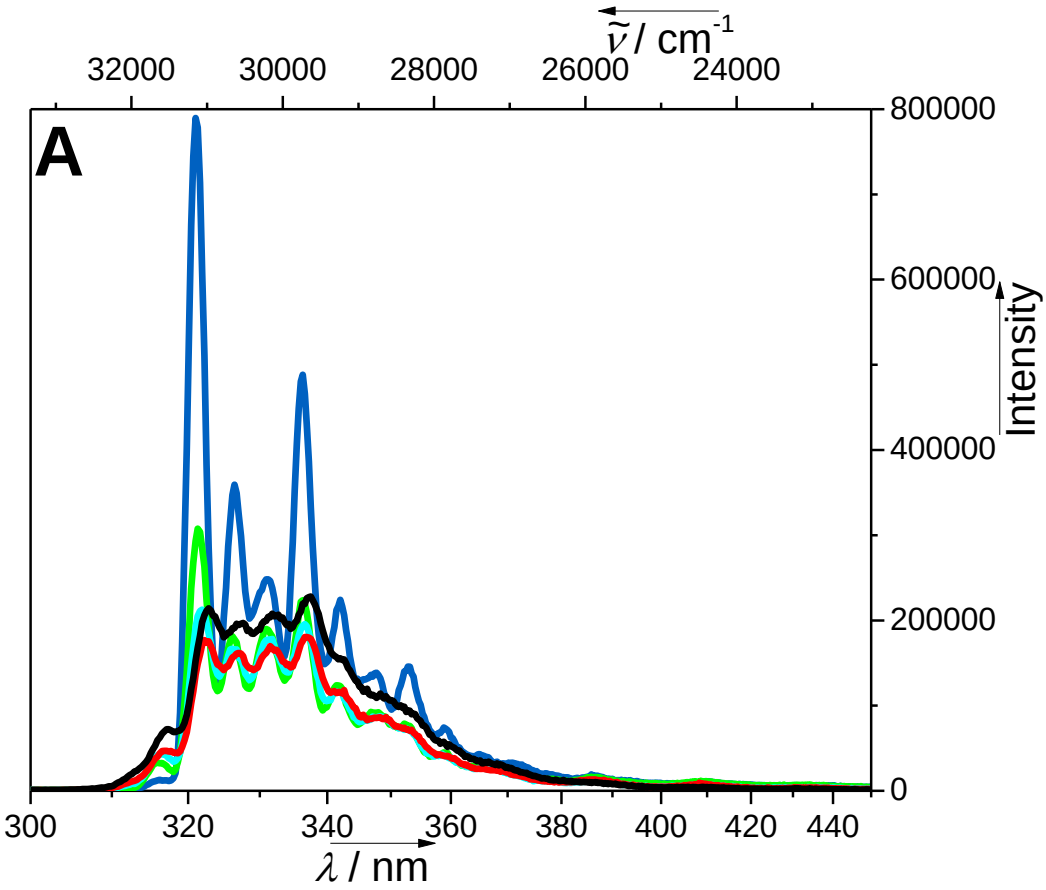

Figure S2A. The fluorescence emission spectra (λ_{exc}= 274 nm) of the thin layer of naphthalene crystals made from the naphthalene solution in methanol after evaporation of the solvent: measured at 77 K (blue line), 133 K (green line), 200 K (cyan line), 253 K (red line), and 295 K (black line).

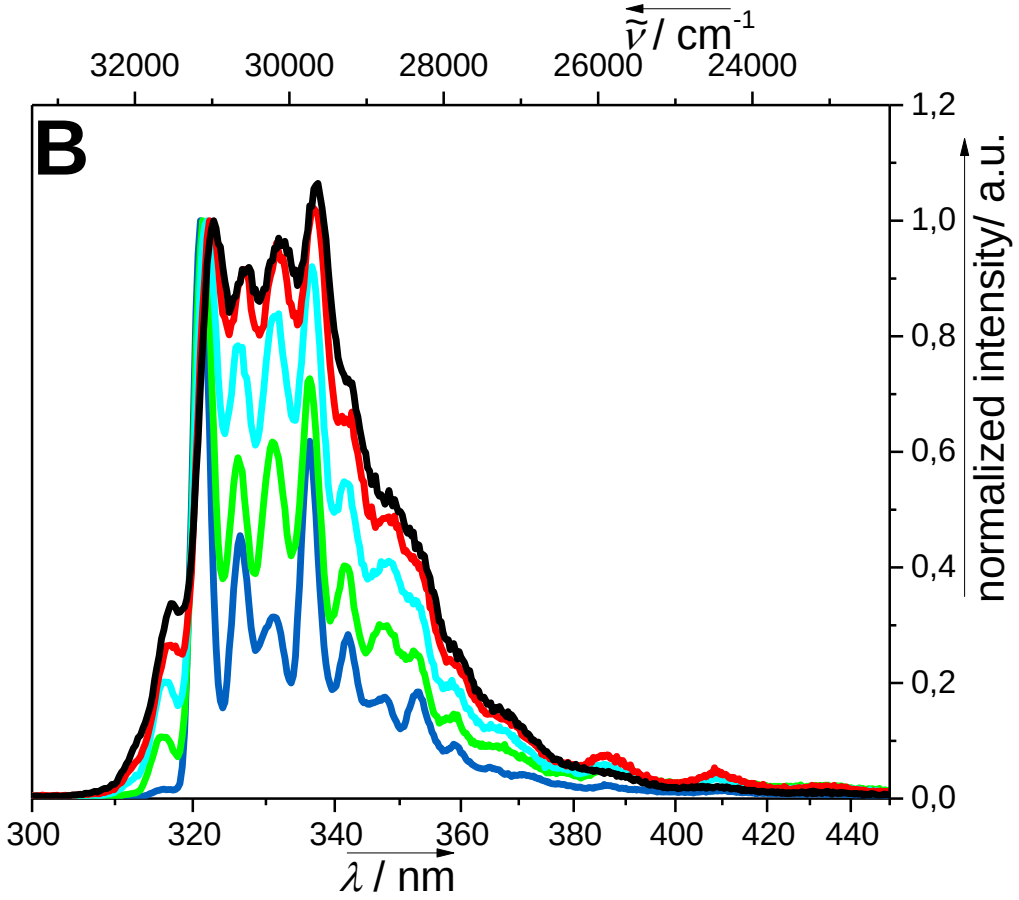

Figure S2B. The normalized fluorescence emission spectra, Fig. S2A, (λ_{exc}= 274 nm) of the thin layer of naphthalene crystals generated from the naphthalene solution in methanol after evaporation of the solvent: measured at 77 K (blue line), 133 K (green line), 200 K (cyan line), 253 K (red line), and 295 K (black line).

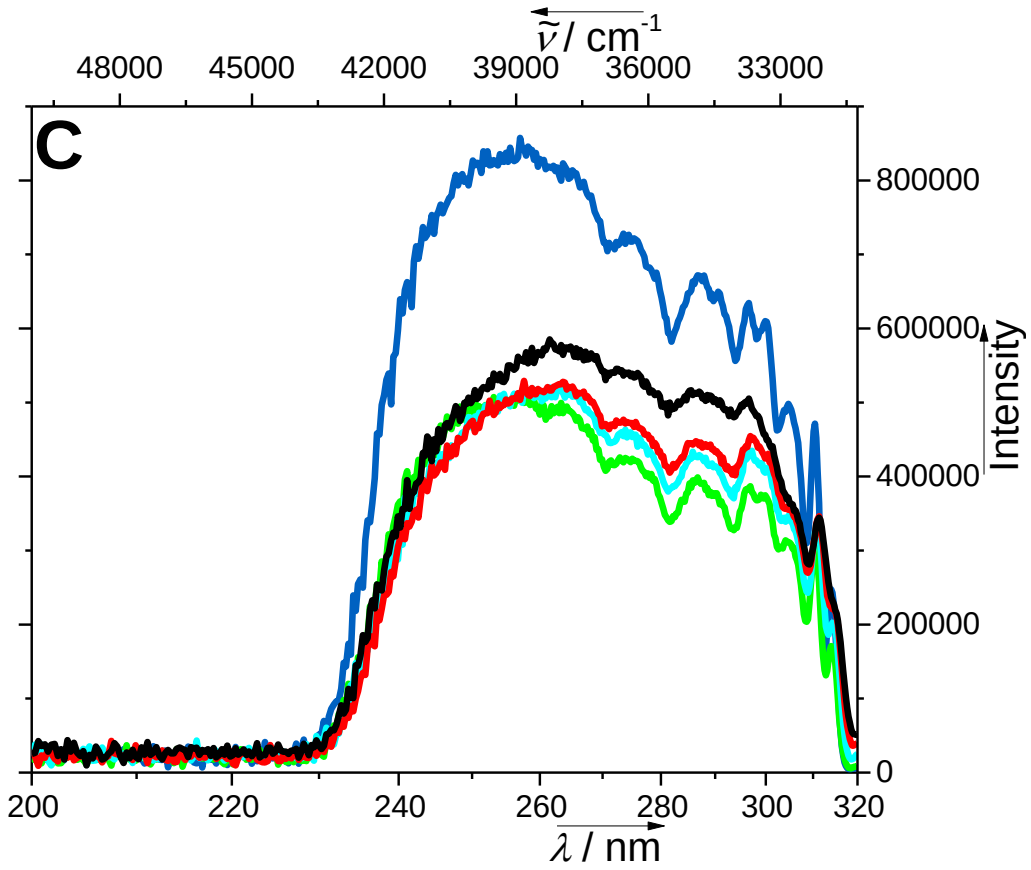

Figure S2C. The fluorescence excitation spectra (λ_{det}= 342 nm) of the thin layer of Np crystals generated from the Np solution in methanol after evaporation of the solvent: measured at 77 K (blue line), 133 K (green line), 200 K (cyan line), 253 K (red line), and 295 K (black line).

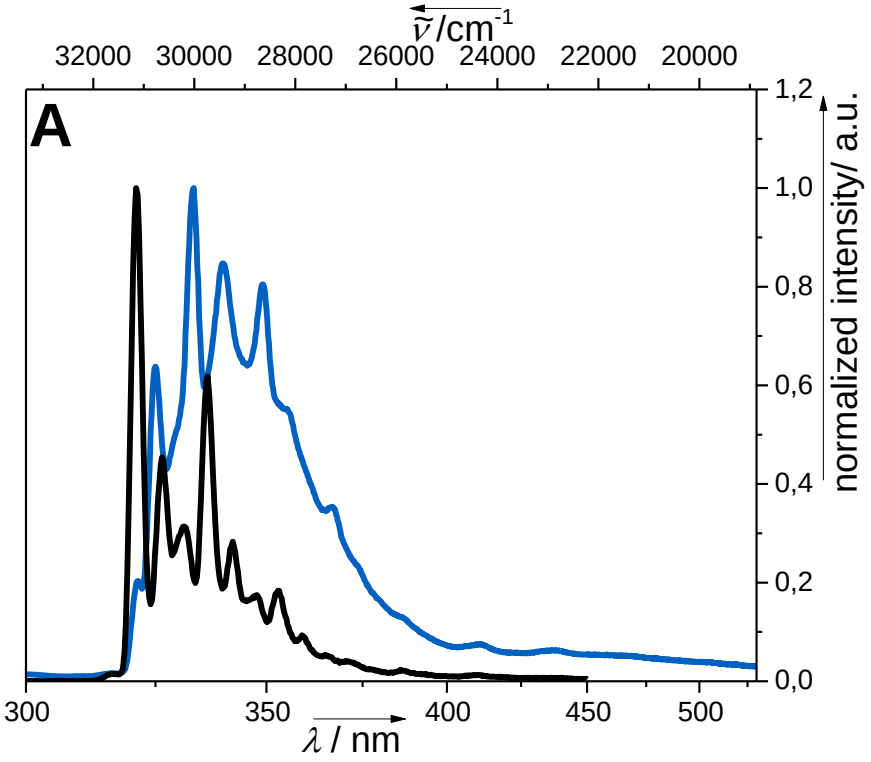

Figure S3A. The normalized fluorescence emission spectra (λ_{exc}= 274 nm) of the fast cooled naphthalene solution (blue line) and the microcrystals in the thin film on glass (black line); both items were measured at 77 K.

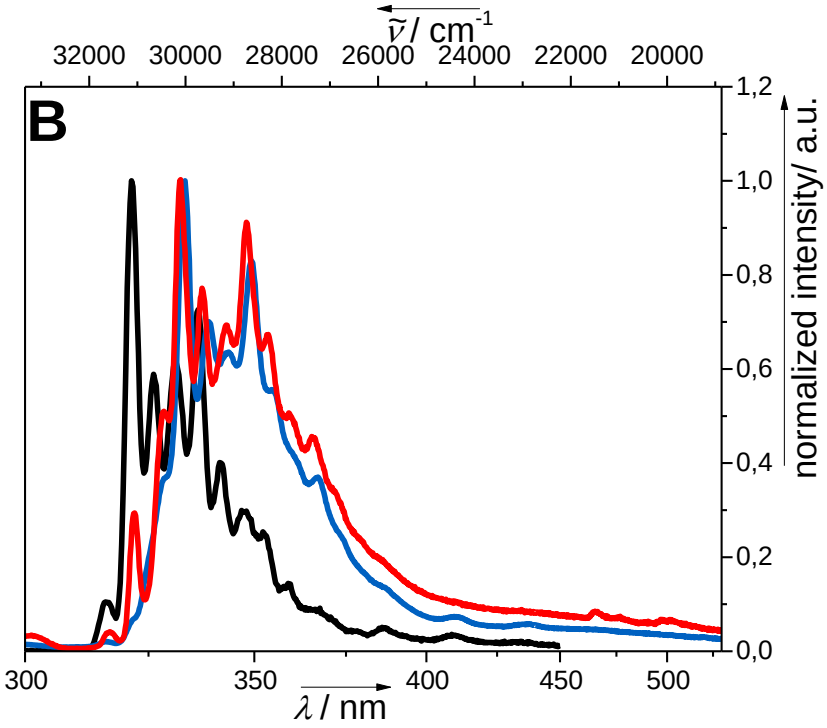

Figure S3B. The normalized fluorescence emission spectra (λ_{exc}= 274 nm) of the fast (blue line) and the slow (red line) cooled naphthalene solutions, completed with the spectrum of the microcrystals in the thin film on glass (black line): all of the items were measured at 133 K.

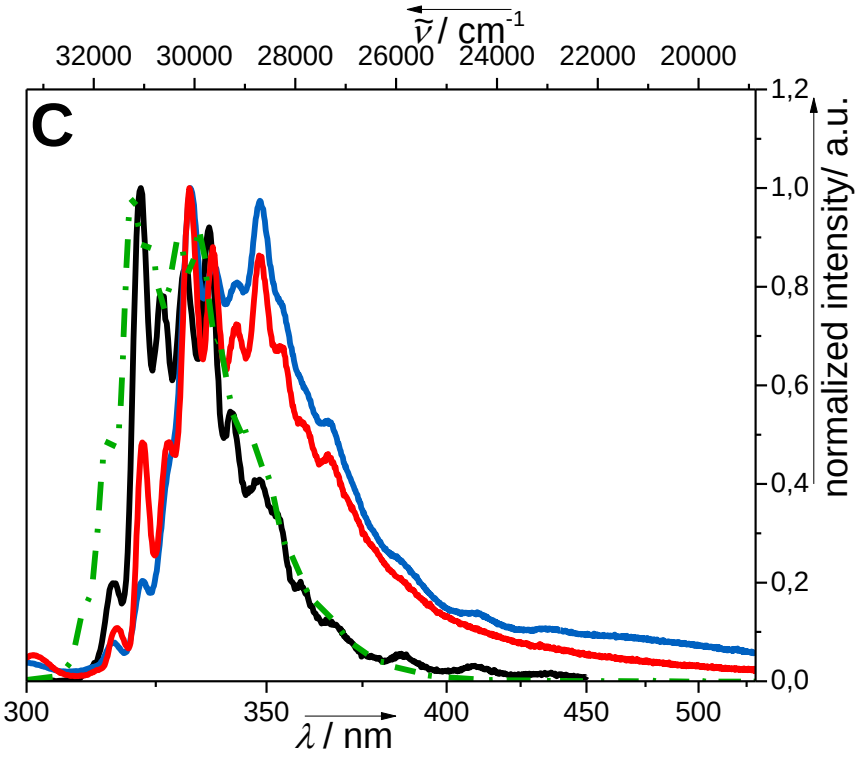

Figure S3C. The normalized fluorescence emission spectra (λ_{exc}= 274 nm) of the fast (blue line) and the slow (red line) cooled naphthalene solutions, completed with the spectrum of the microcrystals in the thin film on glass (black line); each of the items was measured at 200 K. The spectrum of the Np solution (green dash-dot line) obtained at 295 K is shown for comparison.

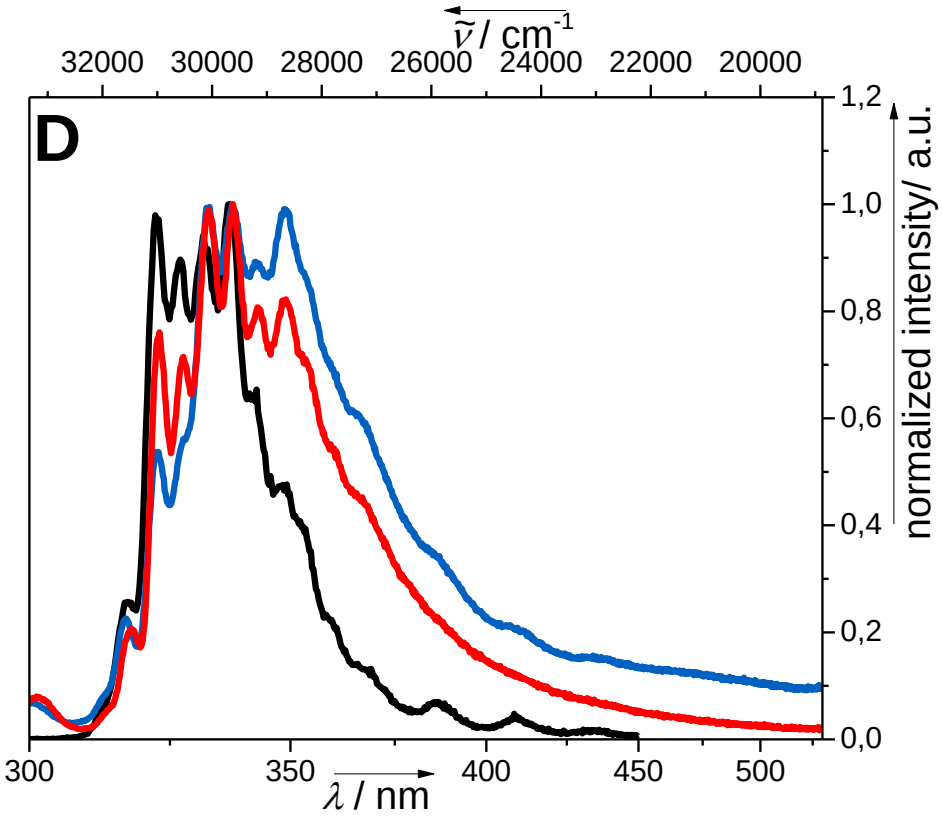

Figure S3D. The normalized fluorescence emission spectra (λ_{exc}= 274 nm) of the fast (blue line) and the slow (red line) cooled naphthalene solutions, completed with the spectrum of the microcrystals in the thin film on glass (black line); each of the items was measured at 253 K.

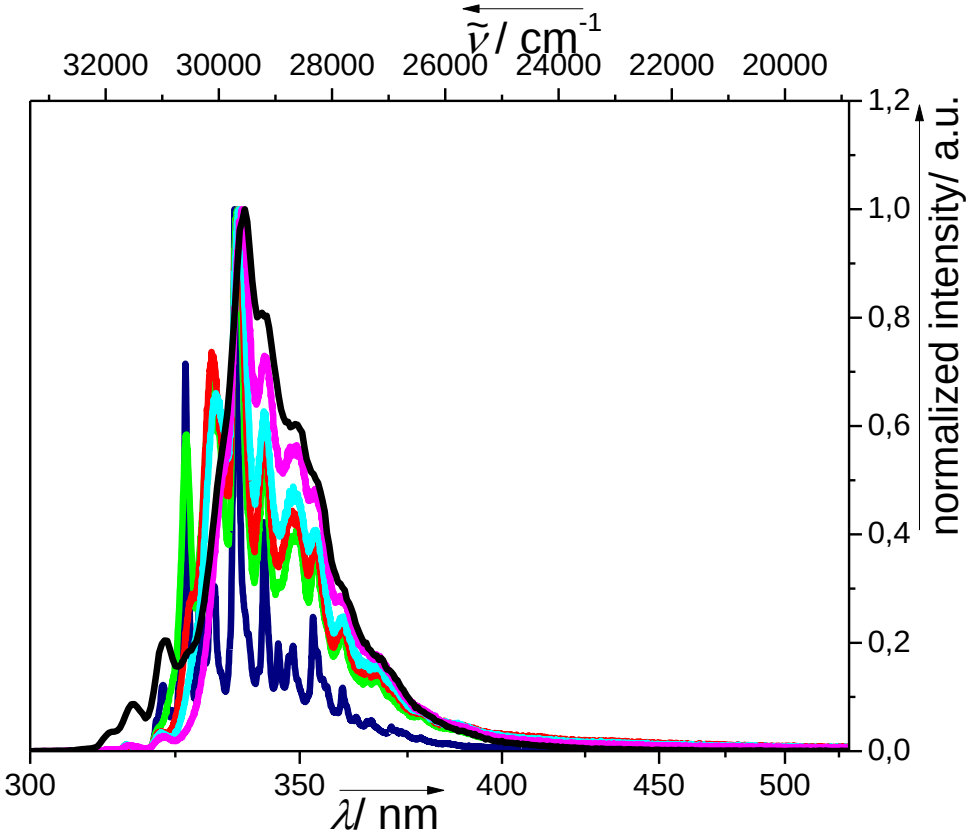

Figure S4. The normalized fluorescence emission spectra (λ_{exc}= 274 nm) of the naphthalene macroscopic-sized crystals measured at 77 K (blue line), 133 K (green line), 173 K (red line), 213 K (cyan line), 253 K (pink line), and 298 K (black line).

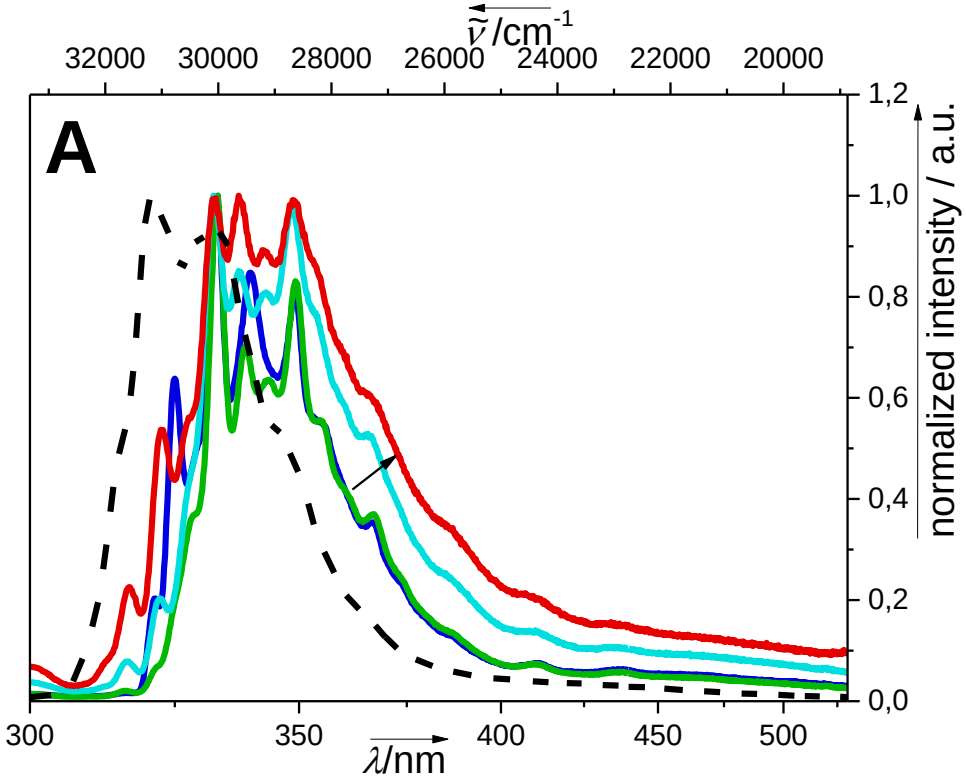

Figure S5A. The normalized fluorescence emission spectra (λ_{exc}= 274 nm) of the fast cooled naphthalene aqueous solutions: measured at 77 K (solid blue line), 133 K (solid green line), 200 K (solid cyan line), 253 K (solid red line); the graph is completed with the spectrum of the solution at 275 K (black dash line).

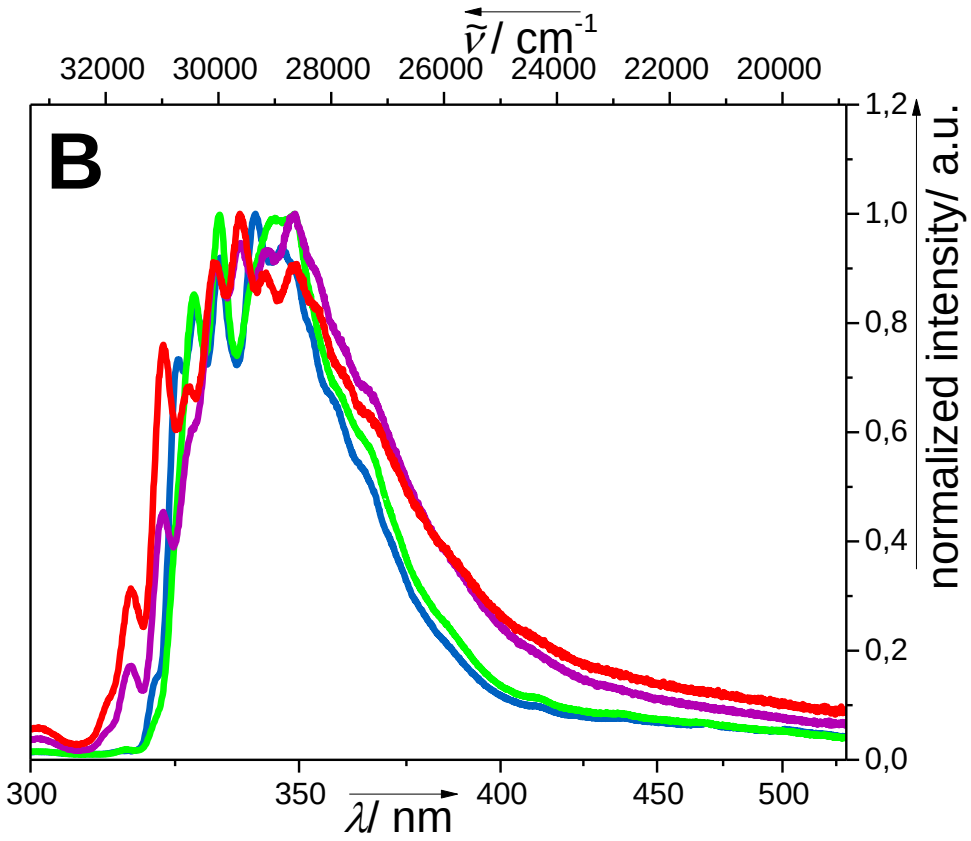

Figure S5B. The normalized fluorescence emission spectra (λ_{exc}= 274 nm) of the fast cooled naphthalene aqueous solutions: measured at 77 K (blue line), 137 K (green line), 257 K (red line), and 270 K (purple line).

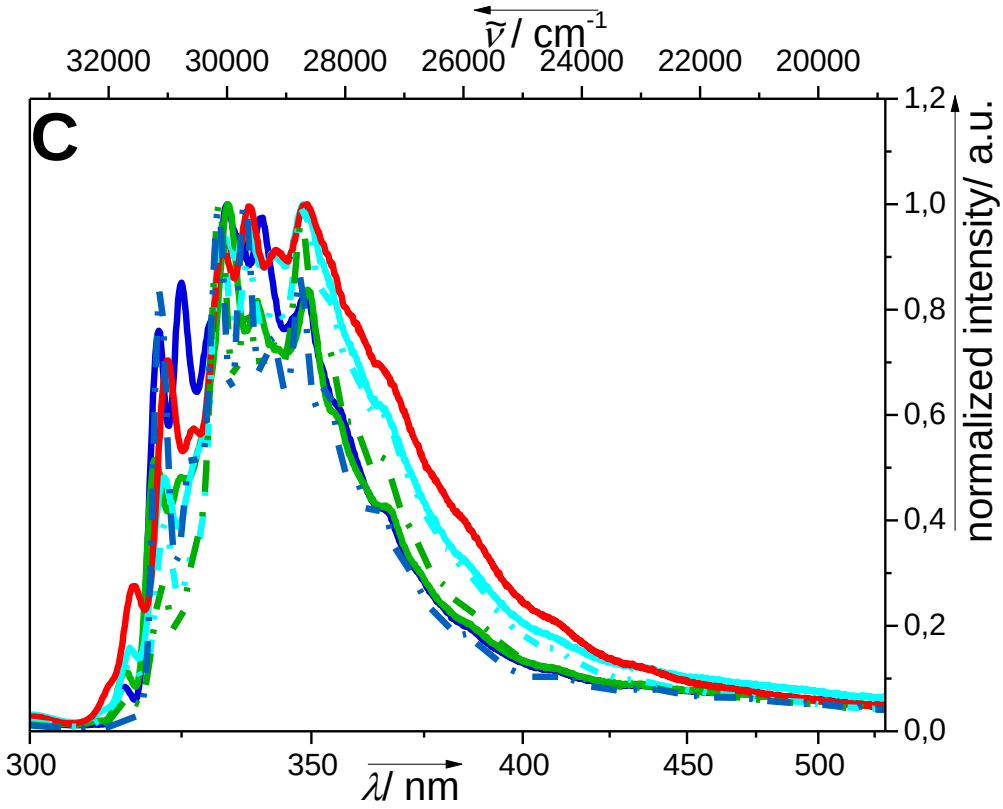

Figure S5C. The normalized fluorescence emission spectra (λ_{exc}= 274 nm) of the fast cooled naphthalene solution. The sample was cycled in temperature and measured consecutively at 77 K (blue line), 133 K (green line), 200 K (cyan line), 253 K (red line), 200 K (cyan dash dot dot line), 133 K (green dash dot dot line), and 77 K (blue dash dot dot line).

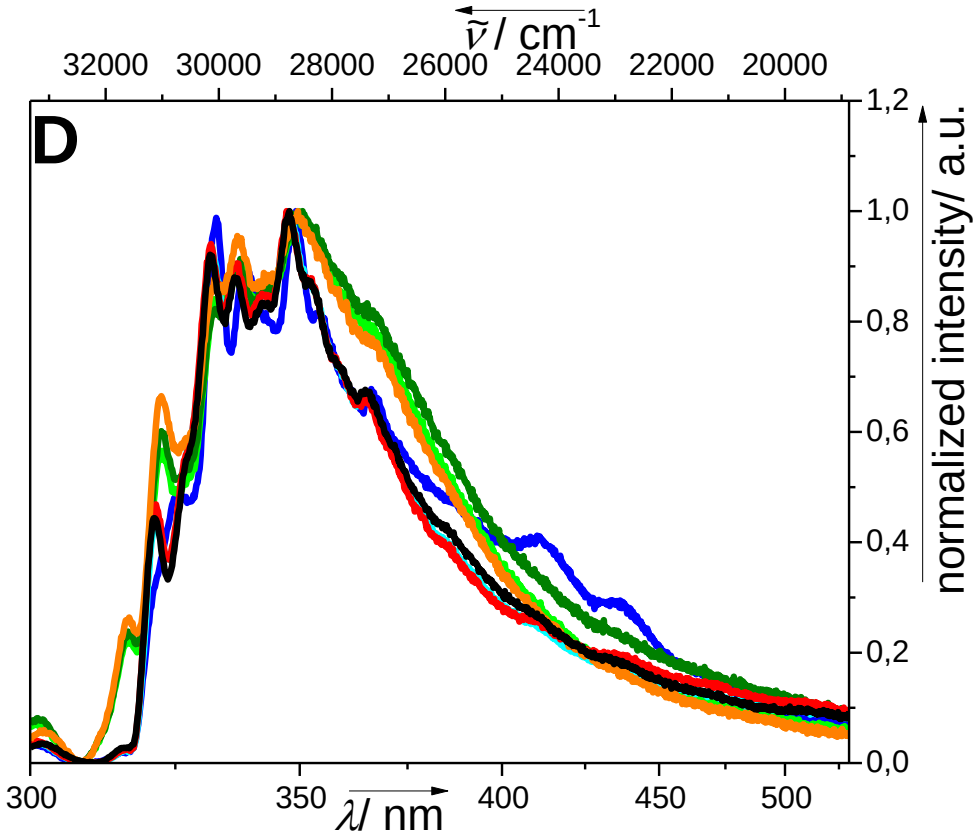

Figure S5D. The normalized fluorescence emission spectra (λ_{exc}= 274 nm) of the fast cooled naphthalene solution. The sample was cycled in temperature and measured consecutively at 77 K (dark blue), 253 K (light green) 77 K (cyan), 253 K (dark green), and 77 K (red). These measurements were performed in one day; after this procedural stage, the sample was stored in a freezer at 253 K for one week and then measured at 253 K (orange) and, after cooling in a cryostat, 77 K (black).

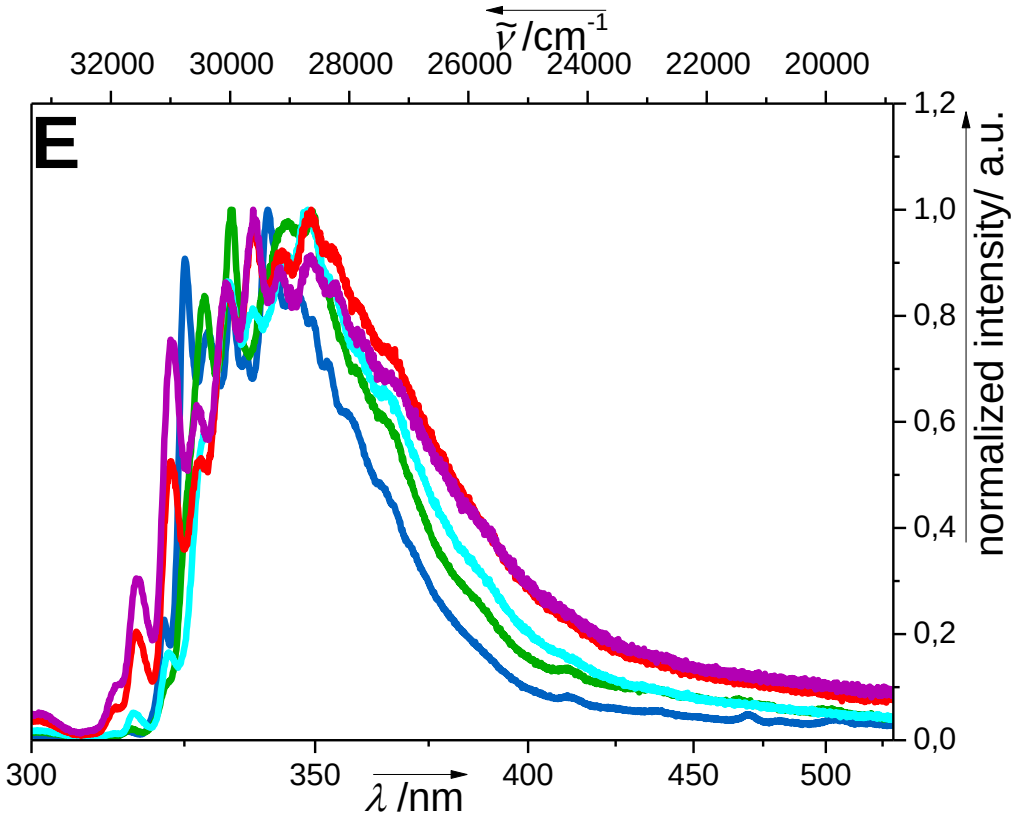

Figure S5E. The normalized fluorescence emission spectra (λ_{exc}= 274 nm) of the fast cooled Np solution: measured at 77 K (blue line), 133 K (green line), 200 K (cyan line), 253 K (red line), and 270 K (purple line).

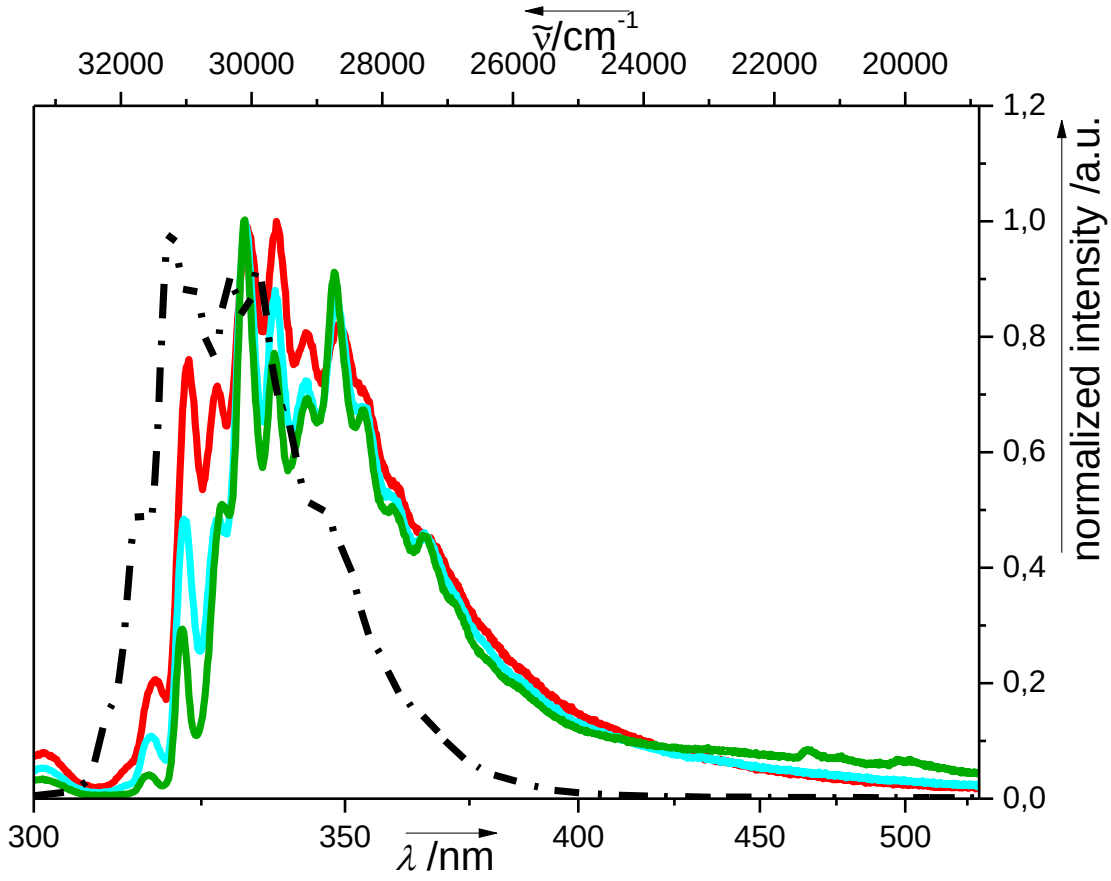

Figure S6. The normalized fluorescence emission spectra (λ_{exc}= 274 nm) of the slow frozen naphthalene solution measured at 253 K (red solid line), 200 K (cyan solid line), and 133 K (green solid line), completed with the spectrum of the melted solution at 275 K (black dash dot line).

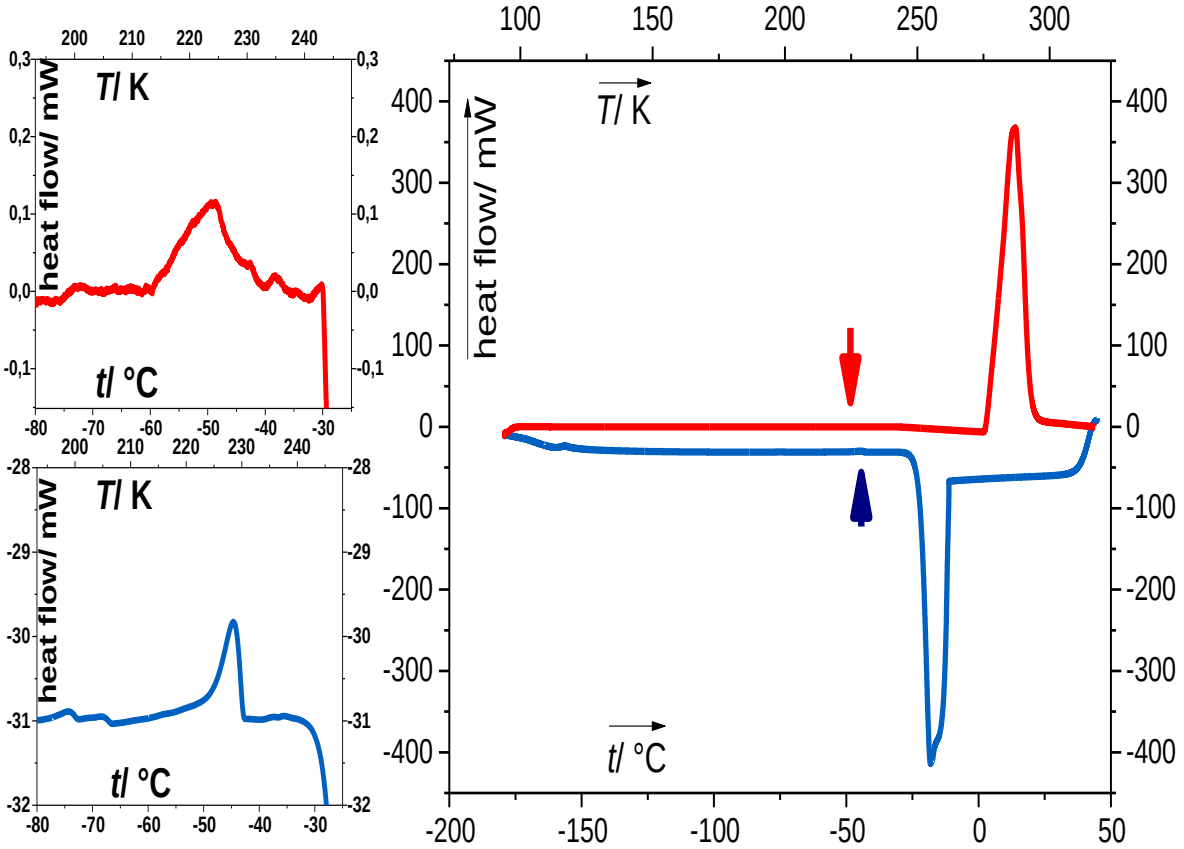

Figure S7. A differential scanning thermogram of the naphthalene solution: cooling and subsequent heating at the rates of 50 K/min (blue line) and 30 K/min (red line), respectively.

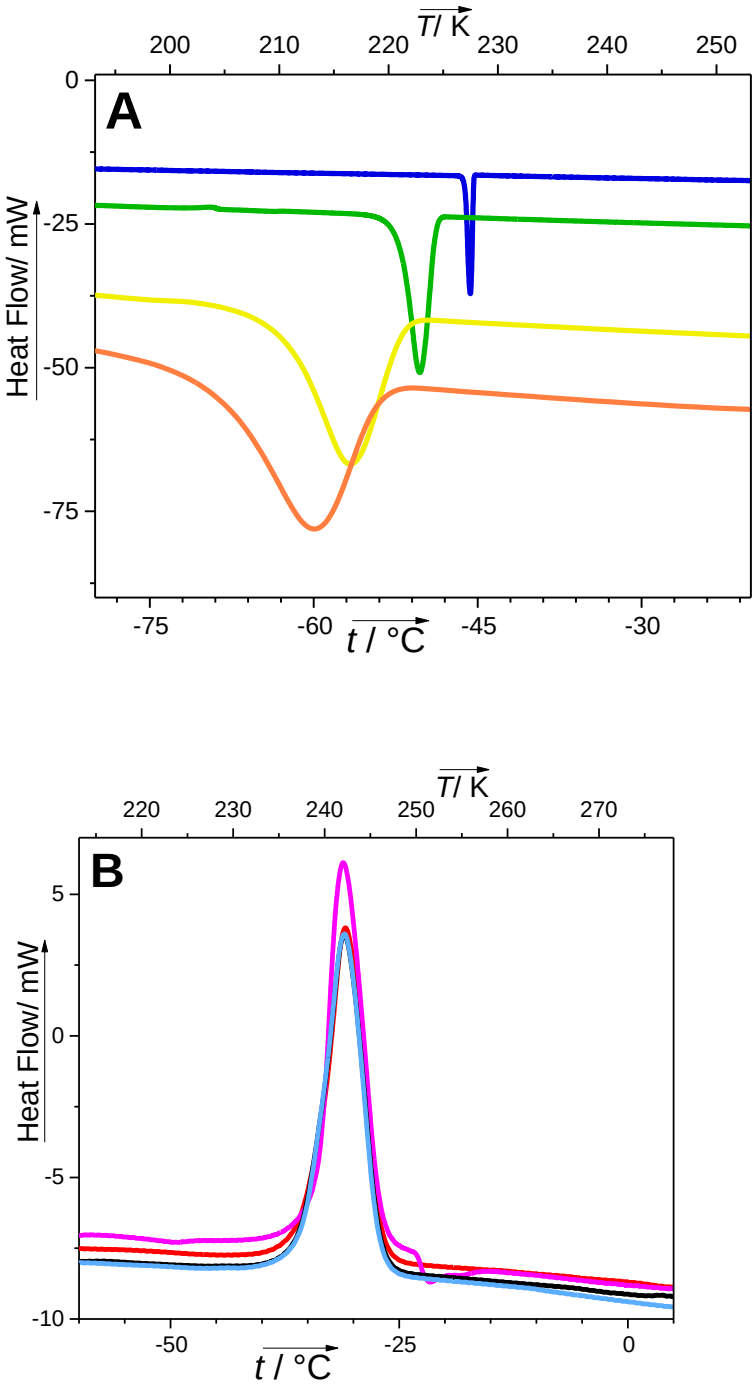

Figure S8. A differential scanning thermogram of the pure 1 - methylnaphthalene. **A)** cooling: dark blue (5 °C/ min), green (30 °C/ min), yellow (100 °C/ min), and orange (150 °C/ min) lines; **B)** heating (red, pink, black, and light blue lines) at the rate of 30 °C/ min.

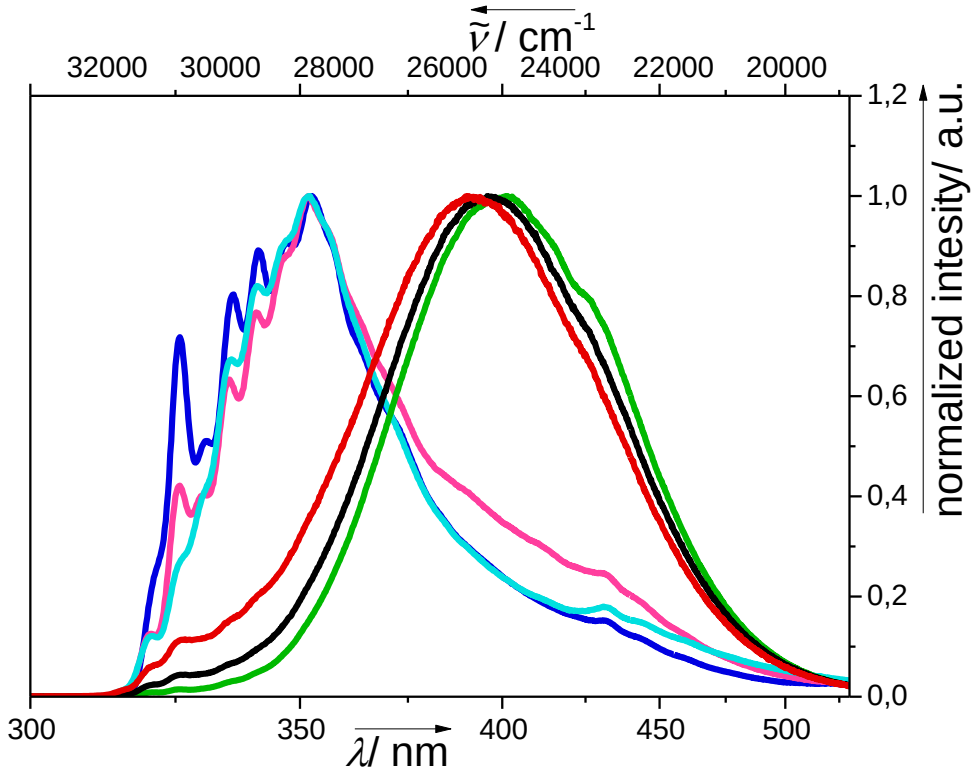

Figure S9. The normalized fluorescence emission spectra (λ_{exc}= 274 nm) of the fast cooled pure 1 – methylnaphthalene: measured at 77 K (blue line), 133 K (pink line), 200 K (cyan line), 240 K (green line), 253 K (black line), and 273 K (red line). The temperatures were measured in the same order as listed.

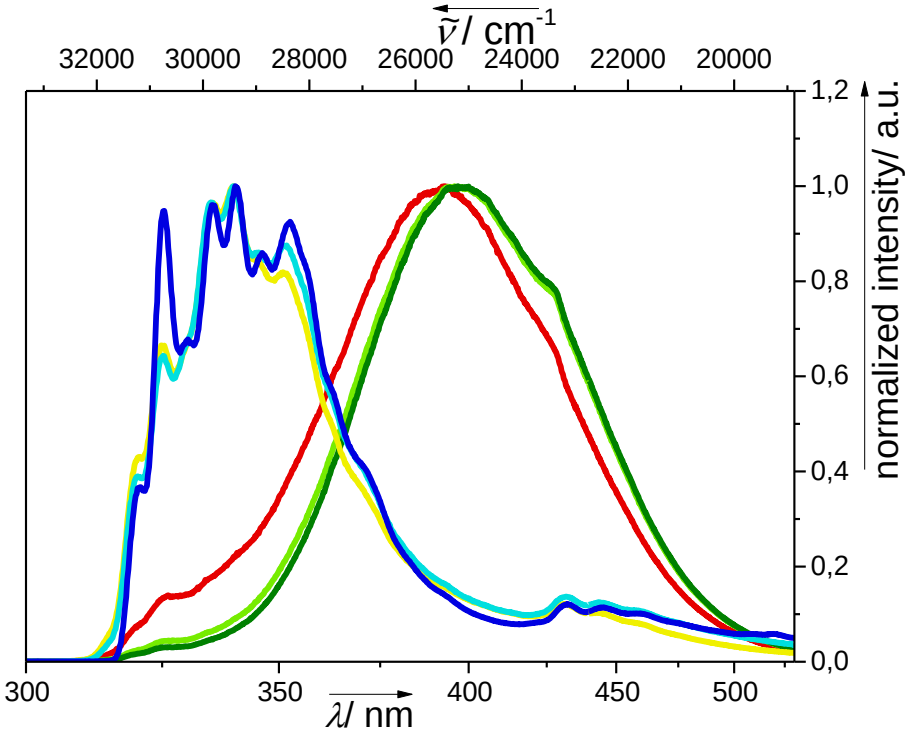

Figure S10. The normalized fluorescence emission spectra (λ_{exc}= 274 nm) of the slow cooled pure 1 - methylnaphthalene measured at 273 K (red line), 250 K (light green line), 243 K (dark green line), 223 K (yellow line), 200 K (cyan line), and 77 K (dark blue line). The temperatures were measured in the same order as listed.

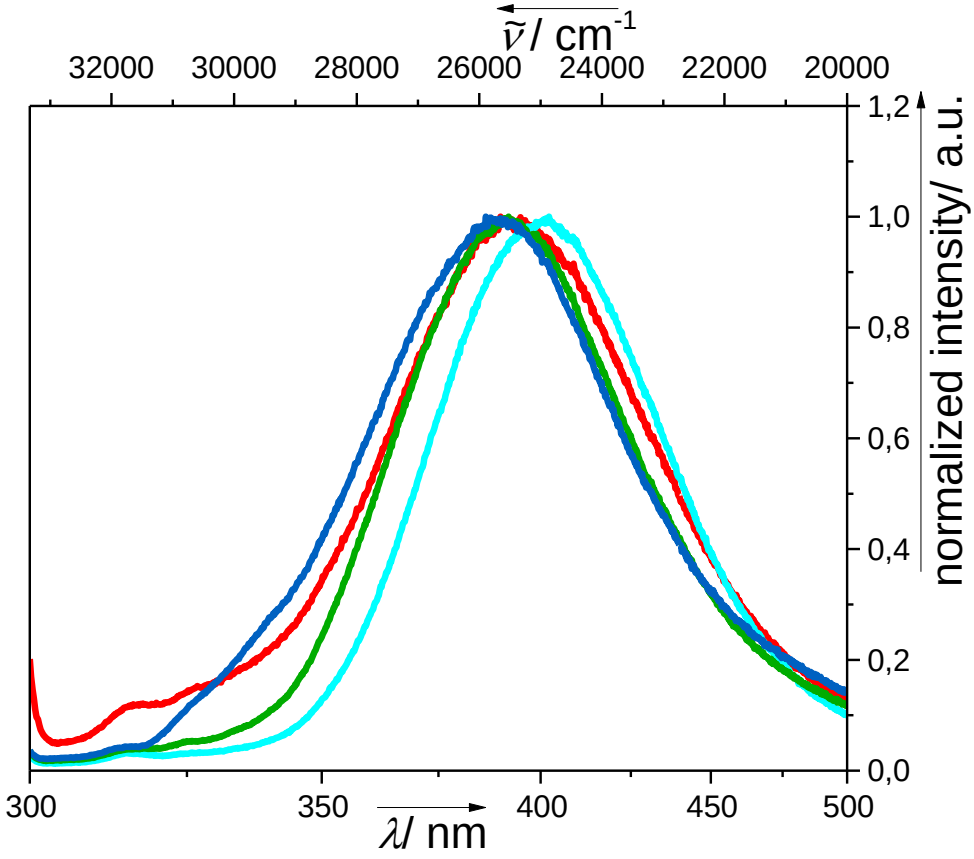

Figure S11. The normalized fluorescence emission spectra (λ_{exc}= 274 nm) of the slowly cooled 1 - methylnaphthalene aqueous solution, measured at 253 K (red line), 200 K (cyan line), 133 K (green line), and 77 K (blue line). The temperatures were measured in the same order as listed.

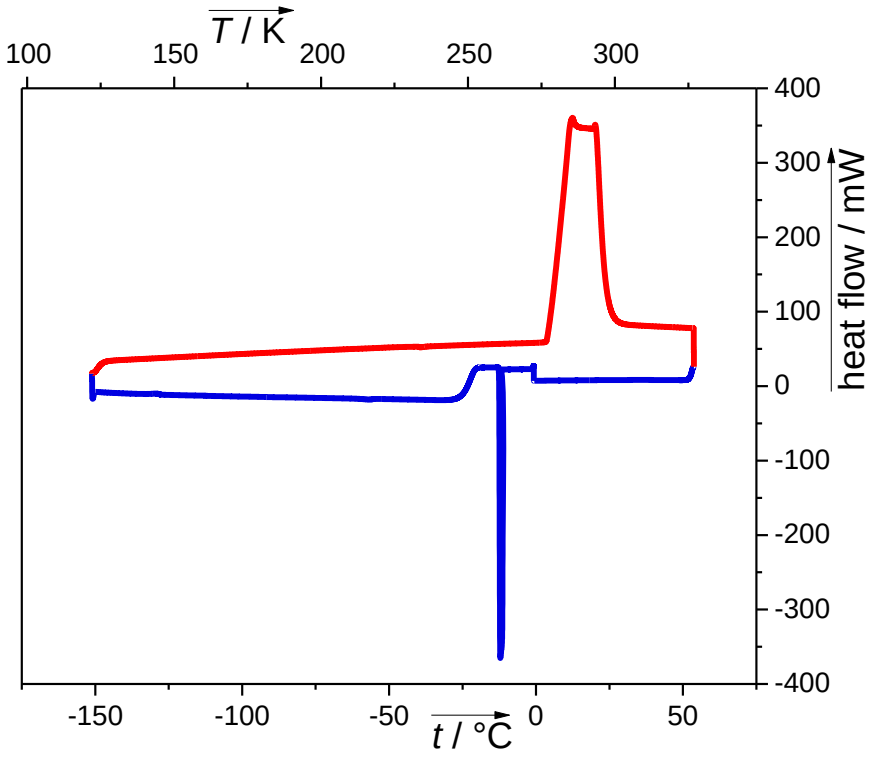

Figure S12. A differential scanning thermogram of the fast frozen 1 - methylnaphthalene solution: cooling (blue line) and subsequent heating (red line). The measurement was performed as follows: 2 min at 60.00°C → to 4 °C (rate 10°C/min) → 1 min at 4°C → to -15°C (rate 2°C/min) → 1 min at - 15°C→ to -150°C (rate 50°C/min) → 1 min at -150°C → to 60°C (rate 30°C/min) → 1min at 60°C.

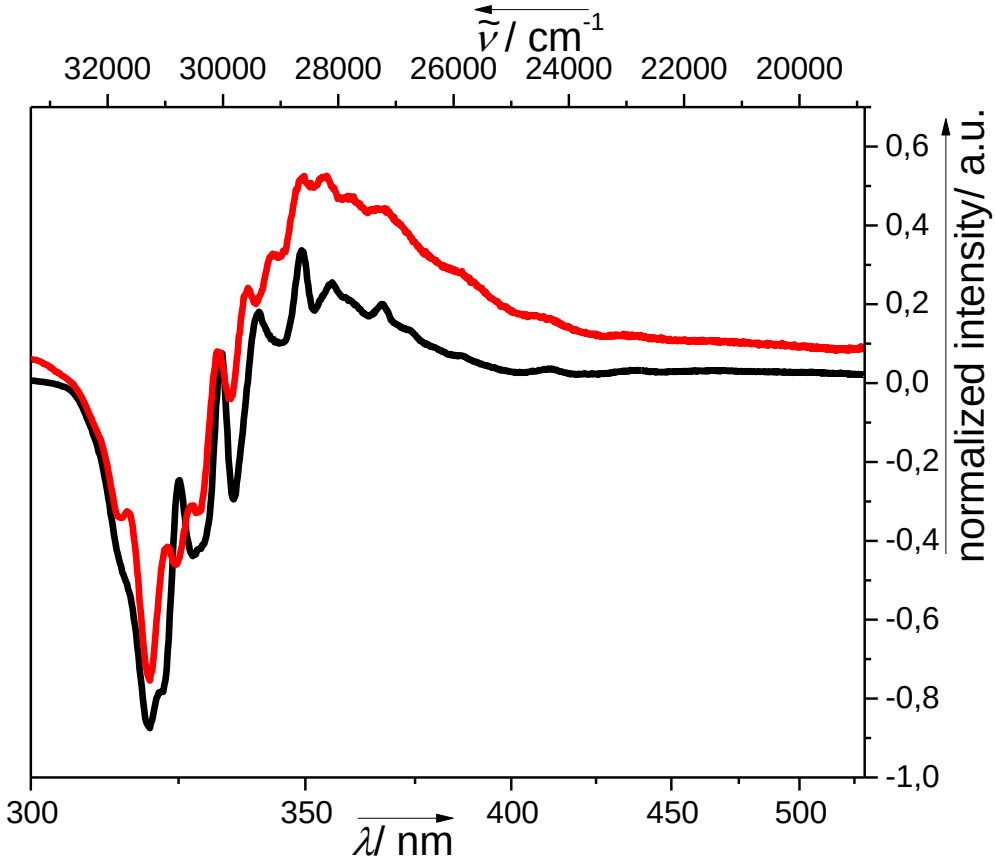

Figure S13. The fluorescence emission spectra (λ_{exc}= 274 nm) calculated by subtracting the spectrum of the naphthalene solution measured at 283 K from that of the fast cooled sample measured at 77 K (black line) and 253 K (red line).

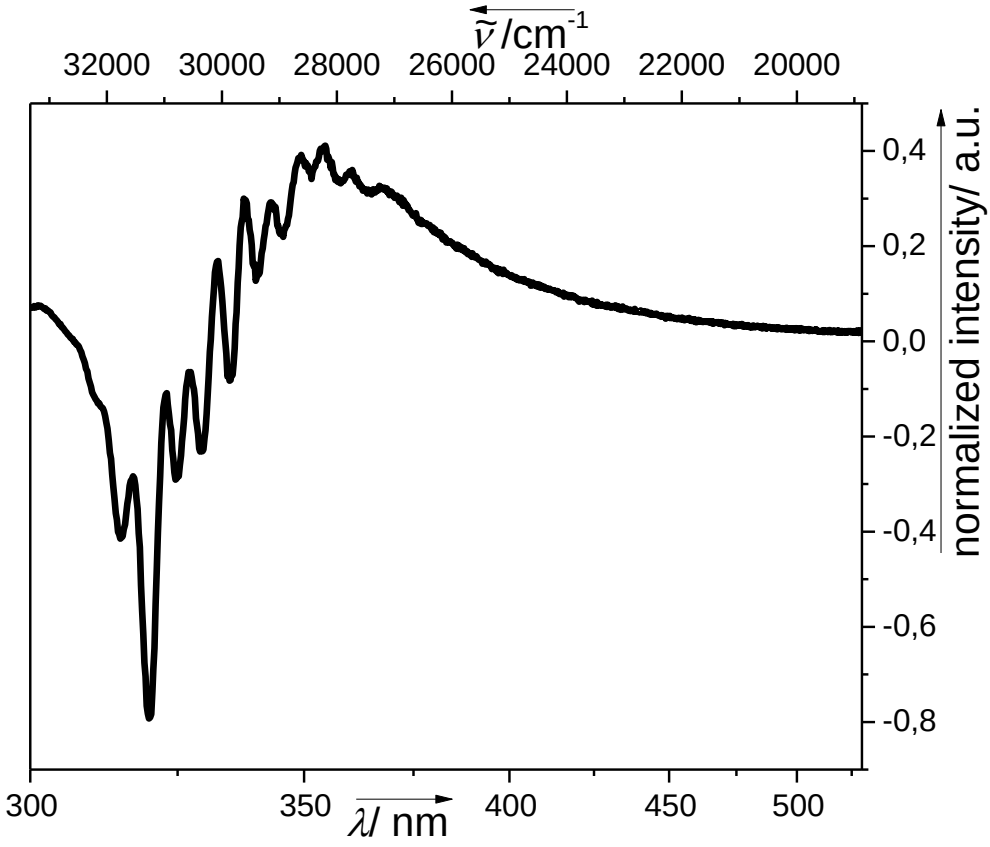

Figure S14. The fluorescence emission spectrum (λ_{exc}= 274 nm) calculated by subtracting the spectrum of the naphthalene solution measured at 293 K from that of the slow cooled sample measured at 253 K.

- **REFERENCES**

1. Ondrušková, G.; Krausko, J.; Stern, J. N.; Hauptmann, A.; Loerting, T.; Heger, D., Distinct Speciation of Naphthalene Vapor Deposited on Ice Surfaces at 253 or 77 K: Formation of Submicrometer-Sized Crystals or an Amorphous Layer. *The Journal of Physical Chemistry C* **2018**, *122*, 11945-11953.