

Supporting information for

Distinguishing the Glass, Crystal, and Quasi-Liquid Layer in 1-Methylnaphthalene by using Fluorescence Signatures

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S1 Slow cooling of the MeNp

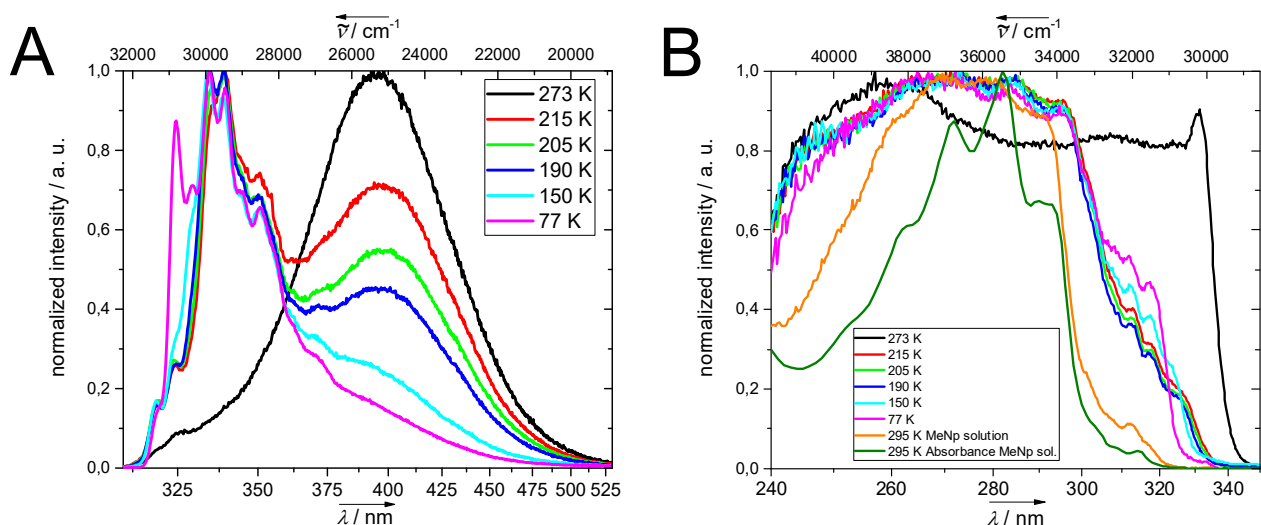


Figure S1. The normalized fluorescence emission (A, $\lambda_{\text{exc}} = 274$ nm) and excitation (B, $\lambda_{\text{det}} = 390$ nm) spectra during the slow-cooling of the MeNp at 273 K (black), 215 K (red), 205 K (green), 190 K (blue), 150 K (cyan), and 77 K (magenta). Represented is also the fluorescence excitation (B, $\lambda_{\text{det}} = 350$ nm) of a 10^{-4} M MeNp solution in cyclohexane (olive) and its absorbance (orange), both at 295 K.

Text S1

The fluorescence emission and excitation spectra of the MeNp are detailed in Figure S1 A and B during the slow cooling from 273 to 77 K, respectively. The emission spectra at 273 K exhibit a broad excimeric band peaking at 395 nm. Upon cooling down to 215 K, the excimeric band reduced its intensity, and the resolved bands of the MeNp crystals appeared on the left-hand side of the spectra. With further cooling, these bands gradually became dominant, while the intensity of the excimeric band decreased even more. Most of the band intensities of the MeNp crystals increased at a similar proportion. Exceptions are the two bands at 325 and 329 nm, which gained substantial intensities at temperatures below 190 K. The maxima of the individual emission bands shown in Figure S1, A were calculated by means of derivative spectroscopy and are reported in Table S2, A.

The excitation spectra of the MeNp are shown in Figure S1, B, and the corresponding excitation maxima revealed through derivation are listed in Table S1. The liquid MeNp at 273 K (black line) exhibited the most distinct band at 331 nm. Once the MeNp has crystallized (at 215 K, in this particular cooling cycle), the excitation spectra began to change notably, as is evident from Figure S1, B: The resolved bands between 250 nm and 317 nm are characteristic of the MeNp crystals, except for the extra band at 326 nm. This band shifted hypsochromically upon cooling to reach 323 nm at 150 K and then disappeared completely at 77 K. Figure S1, B is supplemented with a normalized absorbance and fluorescence excitation spectra of the MeNp solution ($c = 10^{-4}$ M) in cyclohexane.

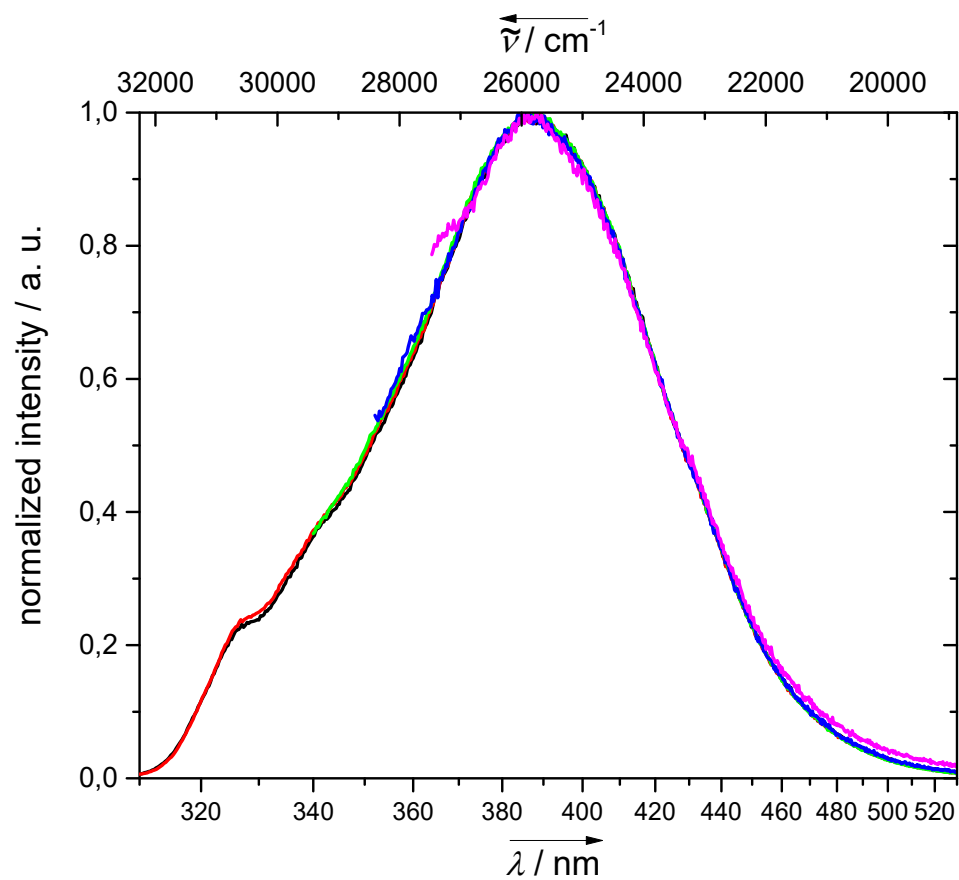


Figure S2. The normalized fluorescence emission of the liquid MeNp at 295 K, with excitations at 274 nm (black line), 300 nm (red line), 330 nm (green line), 340 nm (blue line), and 345 nm (magenta line).

S3 Excitation of the crystals

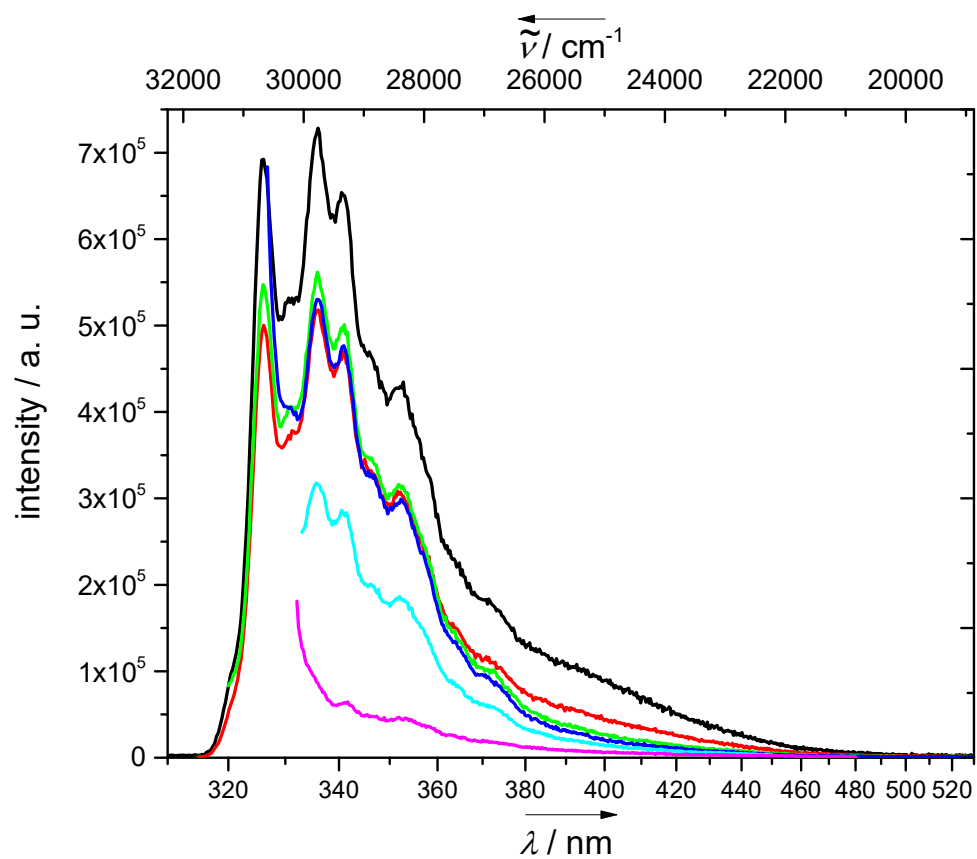


Figure S3. The fluorescence emission spectra of the McNp crystals measured at 77 K, with excitations at 274 nm (black line), 300 nm (red line), 310 (green line), 320 nm (blue line), 322 nm (cyan line), and 325 nm (magenta line).

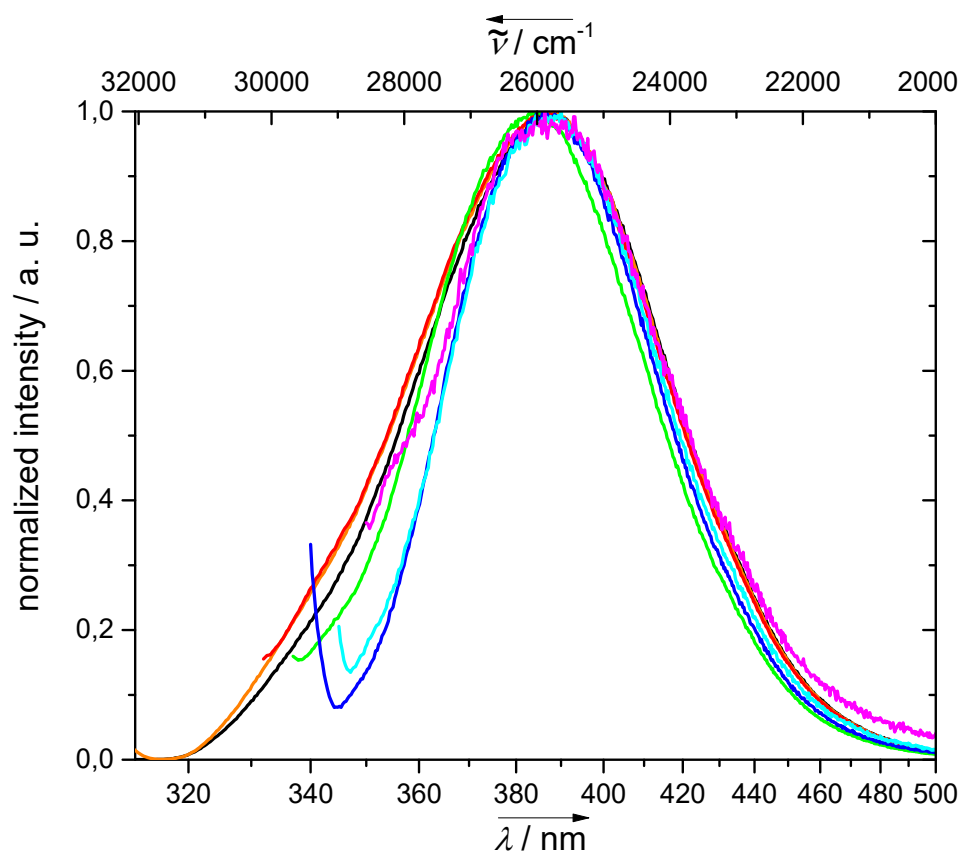


Figure S4. The normalized fluorescence emission spectra of the fast cooled MeNp glass (prepared in liquid methane) at 77 K, with excitations at 274 nm (black line), 300 nm (orange line), 320 nm (red line), 325 nm (green line), 330 nm (blue line), 332 nm (cyan line), and 335 nm (magenta line).

S5 Annealing of the crystals at 200 K

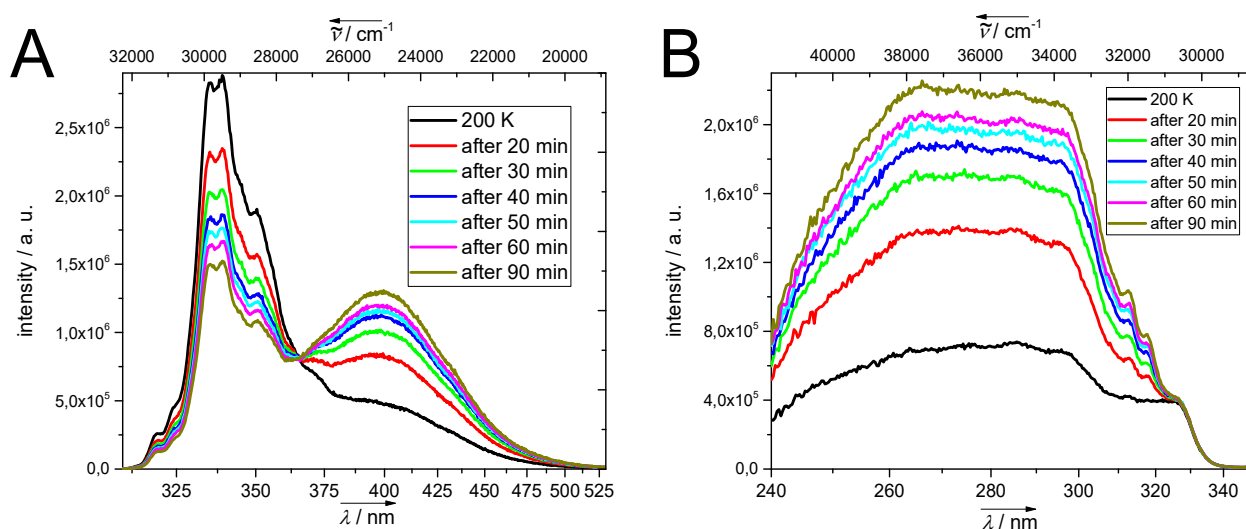


Figure S5. The fluorescence emission (A, $\lambda_{\text{exc}} = 274$ nm) and excitation (B, $\lambda_{\text{det}} = 390$ nm) spectra of the MeNp crystals at 200 K, measured immediately upon reaching the temperature of 200 K (black line) and then after 20 minutes (red line), 30 minutes (green line), 40 minutes (blue line), 50 minutes (cyan line), 60 minutes (magenta line), and 90 minutes (dark yellow).

Text S2

We also conducted a more extensive isothermal annealing experiment where the sample was continuously monitored after it had reached 200 K, recording the fluorescence emission and excitation after 20, 30, 40, 50, 60, and 90 minutes. The resulting fluorescence emission is depicted in Figure S5, A.

From the very beginning, we were able to observe MeNp crystals thanks to their vibrationally resolved bands between 310 and 365 nm, as well as an excimer emission that dominates the spectra between 365 and 500 nm. With passing time, the intensity of the excimeric signal ($\lambda_{\text{max}} = 400$ nm) increased at the expense of the crystals. An isoemissive point between the monomer and the excimer is evident at 365 nm. The fluorescence excitation spectra monitored during this process are shown in Figure S5, B. The resolved band maxima can be reviewed in Table S1. As the time progressed further, the intensities of all the bands in the excitation spectra kept increasing continuously, except for the band at 326 nm, which remained at a comparable level.

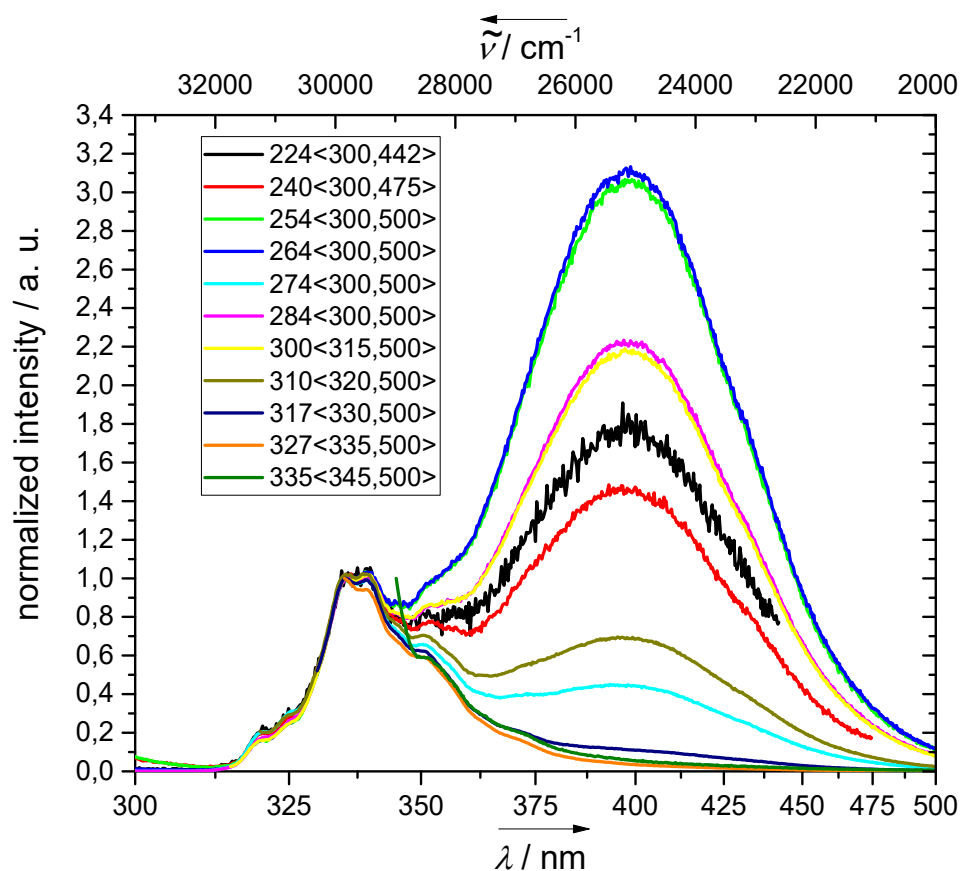


Figure S6. The normalized fluorescence emission of the MeNp crystals at 220 K (slow cooled from 295 K), with excitations at 224 nm (black line), 240 nm (red line), 254 nm (green line), 264 nm (blue line), 274 nm (cyan line), 284 nm (magenta line), 300 nm (yellow line), 310 nm (dark yellow line), 317 nm (navy line), 327 nm (orange line), and 335 nm (olive line). The emission and excitation slits were maintained at a constant level during the measurements.

S7 Proportion of the fluorescence emission intensities of the excimer maxima (398 nm) divided by those of the monomer (335 nm)

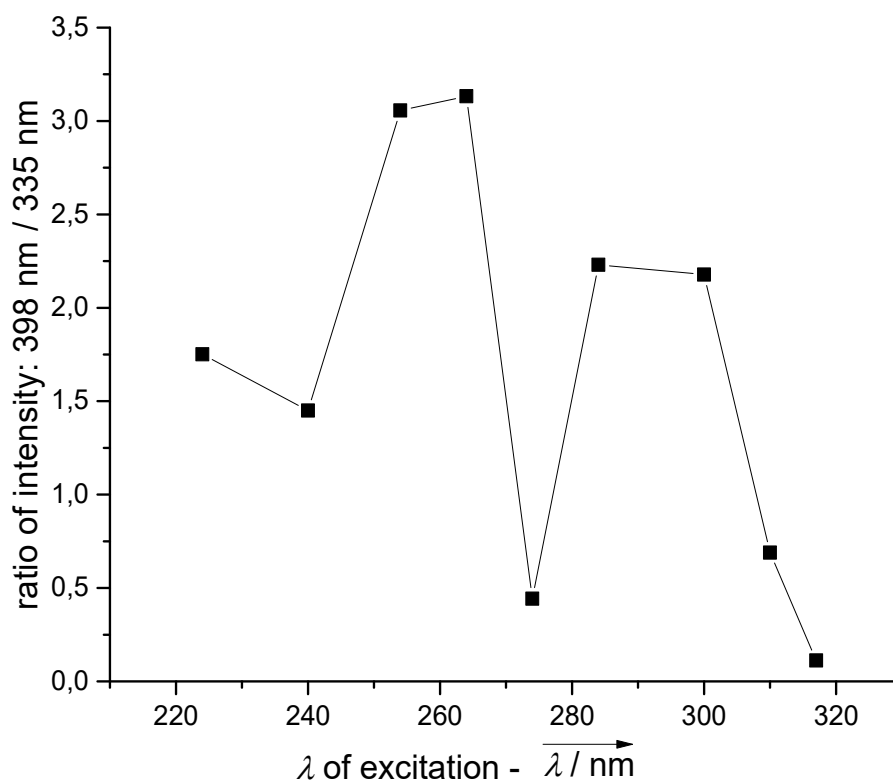


Figure S7. The proportion of the fluorescence emission intensity of the excimer maxima (398 nm) divided by those of the monomer (335 nm) of the MeNp crystals, all measured at 220 K as a function of the excitation wavelength; the relevant spectra are shown in Figure S6.

S8 Heating of the glass emission spectra: 77 – 150 K

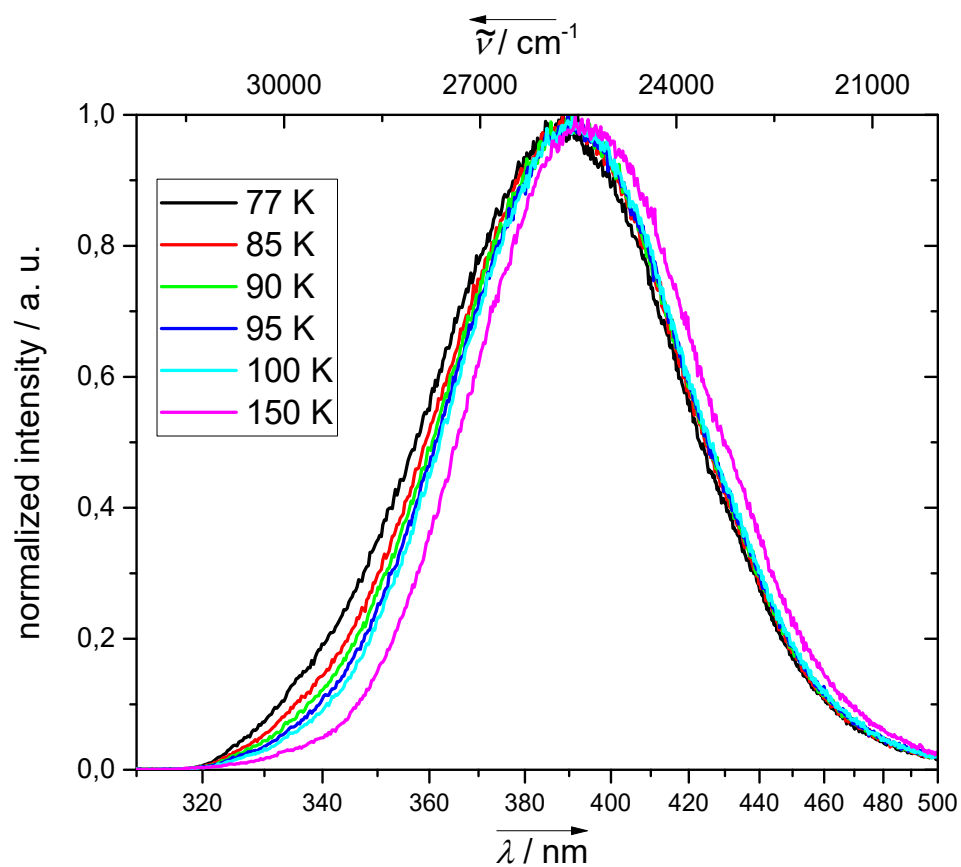


Figure S8. The normalized fluorescence emission spectra ($\lambda_{\text{exc}} = 274 \text{ nm}$) of the MeNp glass (prepared in liquid methane) at 77 K (black line) and after heating to 85 K (red line), 90 K (green line), 95 K (blue line), 100 K (cyan line), and 150 K (magenta line).

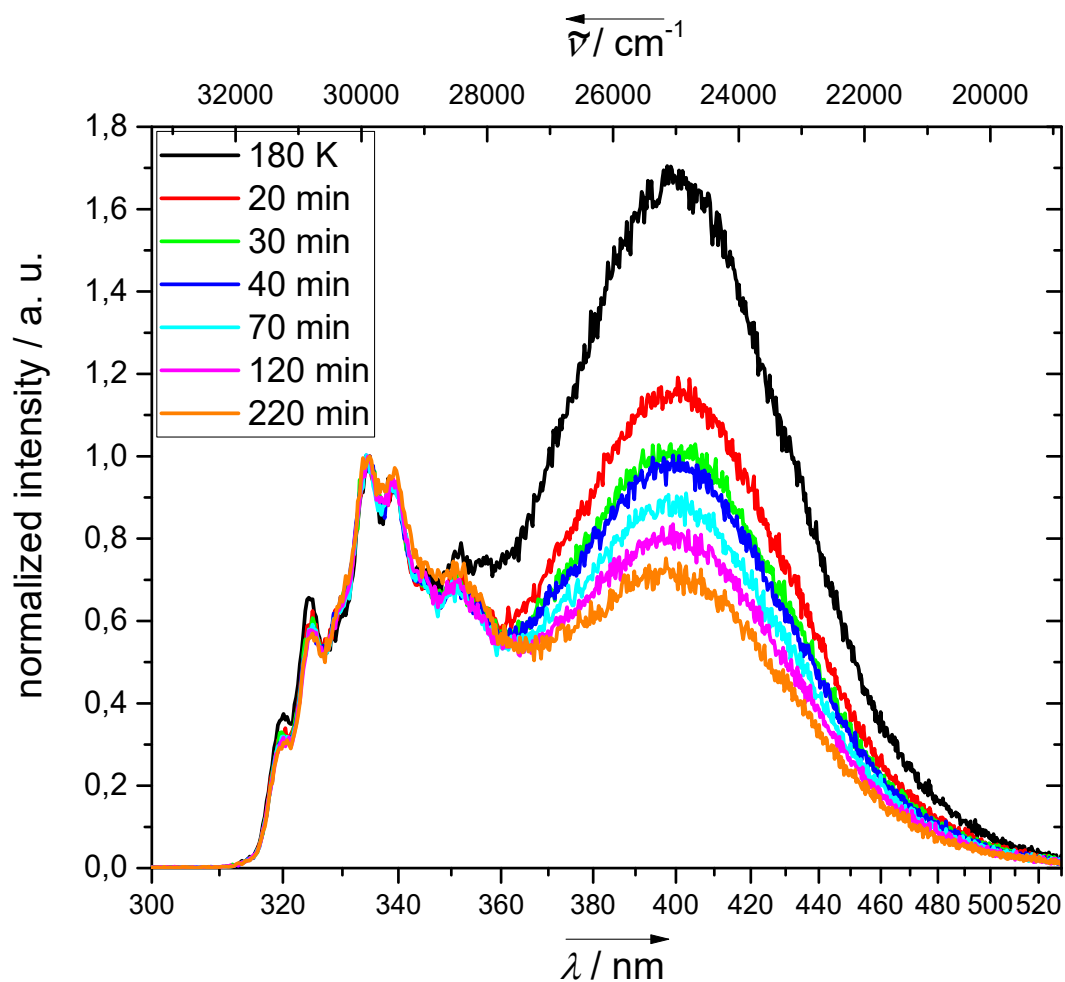


Figure S9. The fluorescence emission spectra ($\lambda_{\text{exc}} = 274 \text{ nm}$) of the crystallization of the MeNp glass (fast frozen in methane) at 180 K (heated from 77 K), measured immediately upon the temperature of 180 K (black line) and then after 20 minutes (red line), 30 minutes (green line), 40 minutes (blue line), 70 minutes (cyan line), 120 minutes (magenta line), and 220 minutes (orange).

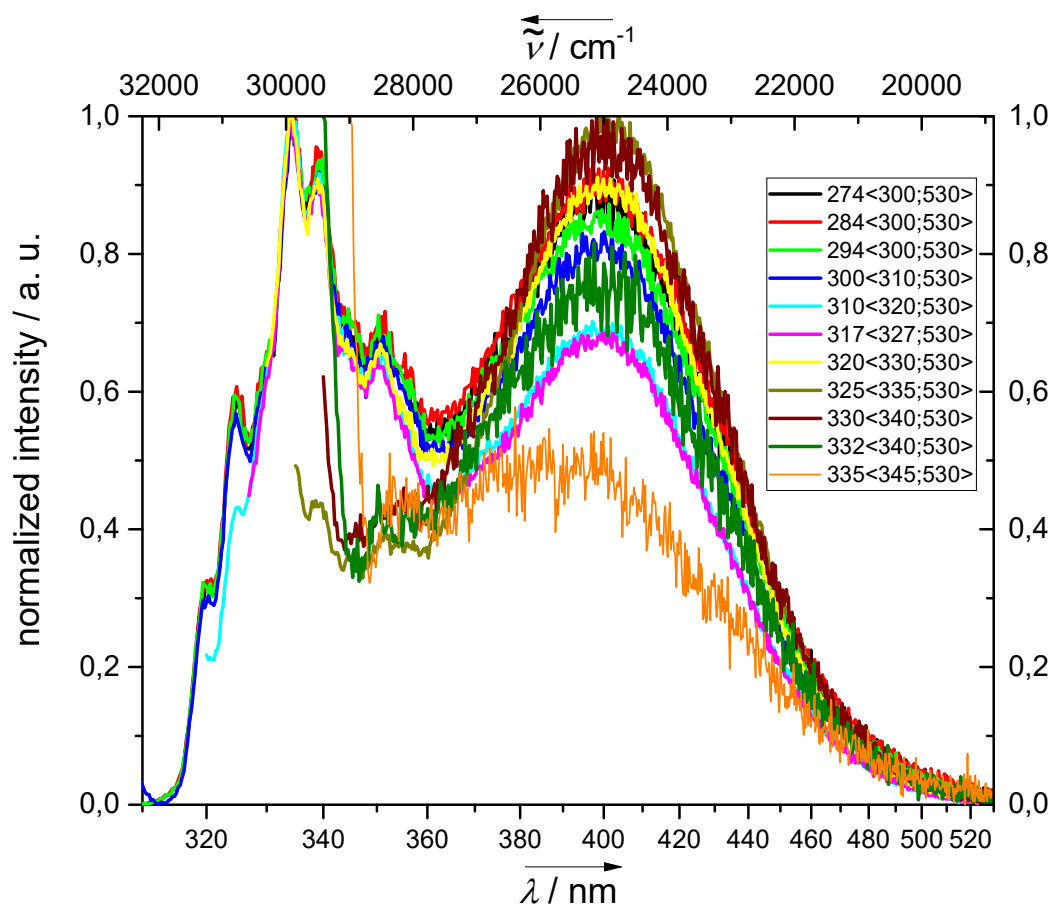


Figure S10. The fluorescence emission spectra of the crystallization of the MeNp glass (frozen in liquid methane), measured at 180 K (heated from 77 K). The excitations were executed at 274 nm (black line), 284 nm (red line), 294 nm (green line), 300 nm (blue line), 310 nm (cyan line), 317 nm (magenta line), 320 nm (yellow line), 325 nm (dark yellow line), 330 nm (wine line), 332 nm (olive line), and 335 nm (orange line).

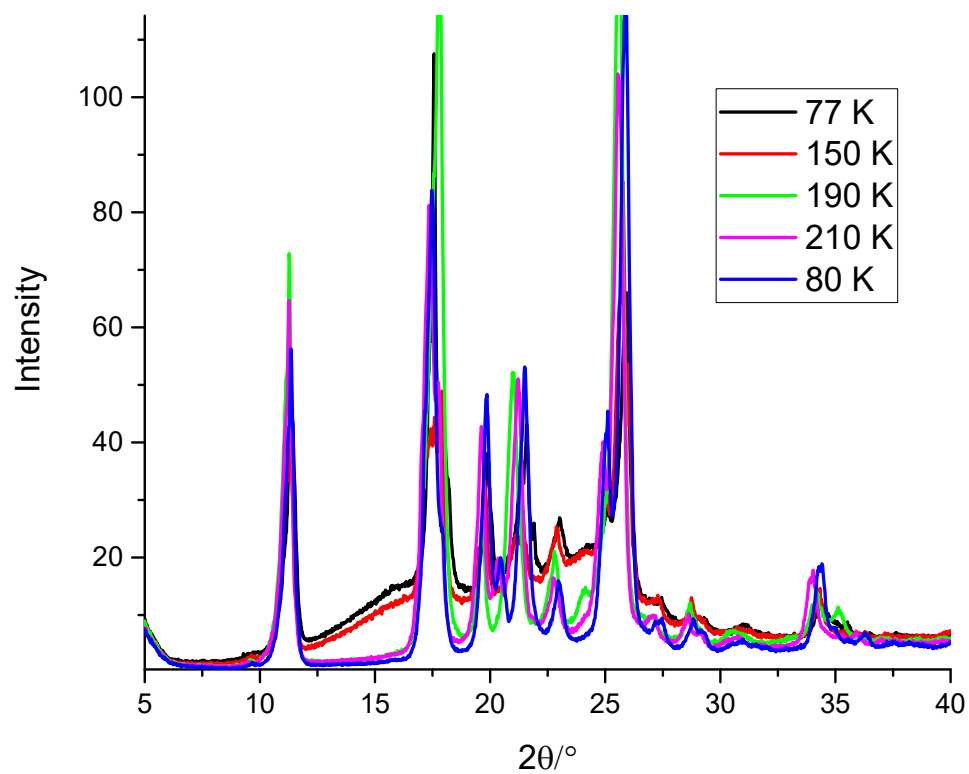


Figure S11. The X-ray diffractograms of the MeNp fast cooled in liquid nitrogen, measured at 77 K (black line) and after heating to 150 K (red line), 190 K (green line), and 210 K (magenta line) to be cooled down from 210 K to 80 K (blue line).

S12 XRD of the MeNp liquid, and the subtraction of the final diffractogram at 80 K from the initial one at 77 K

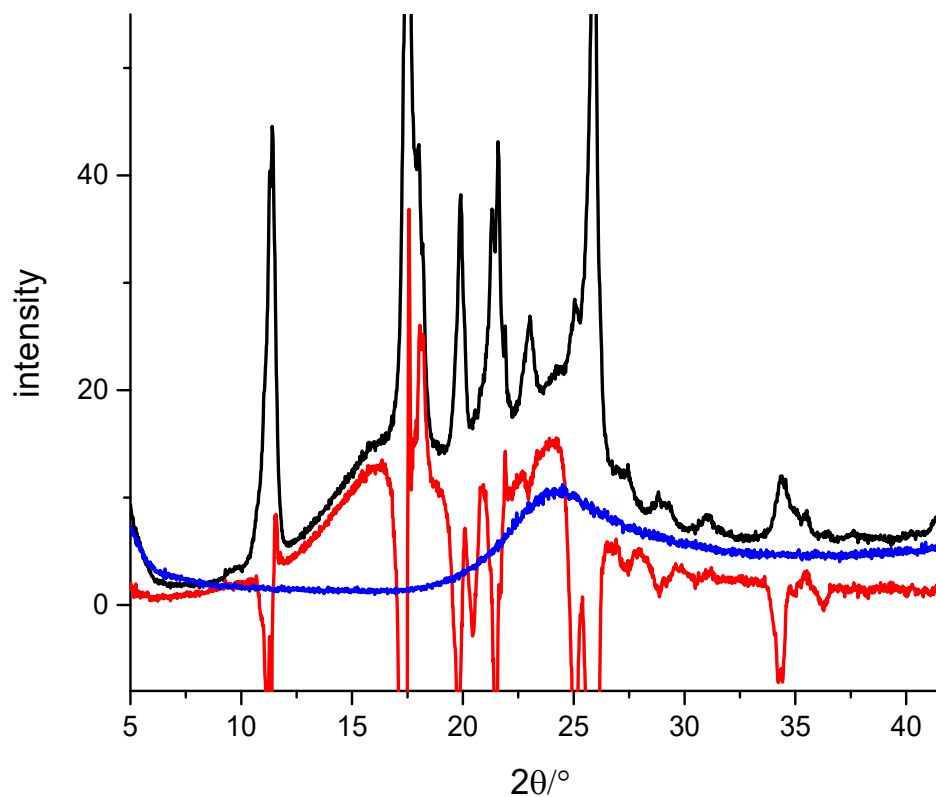


Figure S12. The X-ray diffractograms of the MeNp fast cooled in liquid nitrogen, measured at 77 K (black line), and the subtraction of the spectrum at 80 K (with the MeNp heated to 210 K and then cooled back down) from the original spectrum at 77 K (red line); the remaining curve represents the liquid MeNp at 260 K (blue line).

S13 Proportion of the 320/273 nm fluorescence excitation intensities of the MeNp crystals at the indicated temperatures

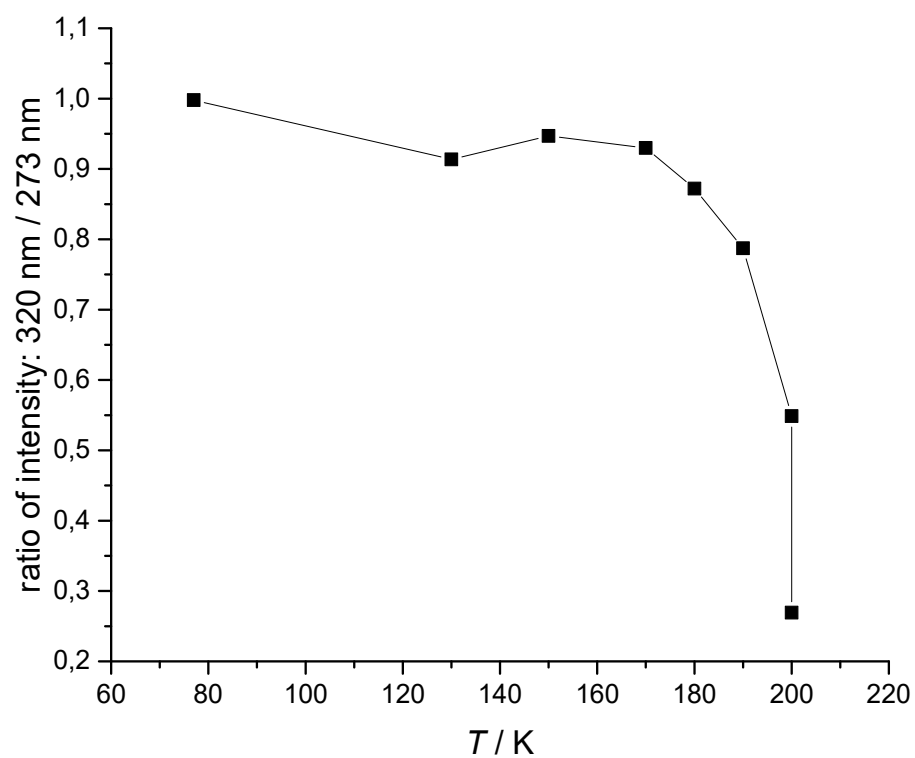


Figure S13. The proportion of the 320/273 nm fluorescence excitation intensities ($\lambda_{\text{det}} = 390$ nm) of the MeNp crystals at the indicated temperatures.

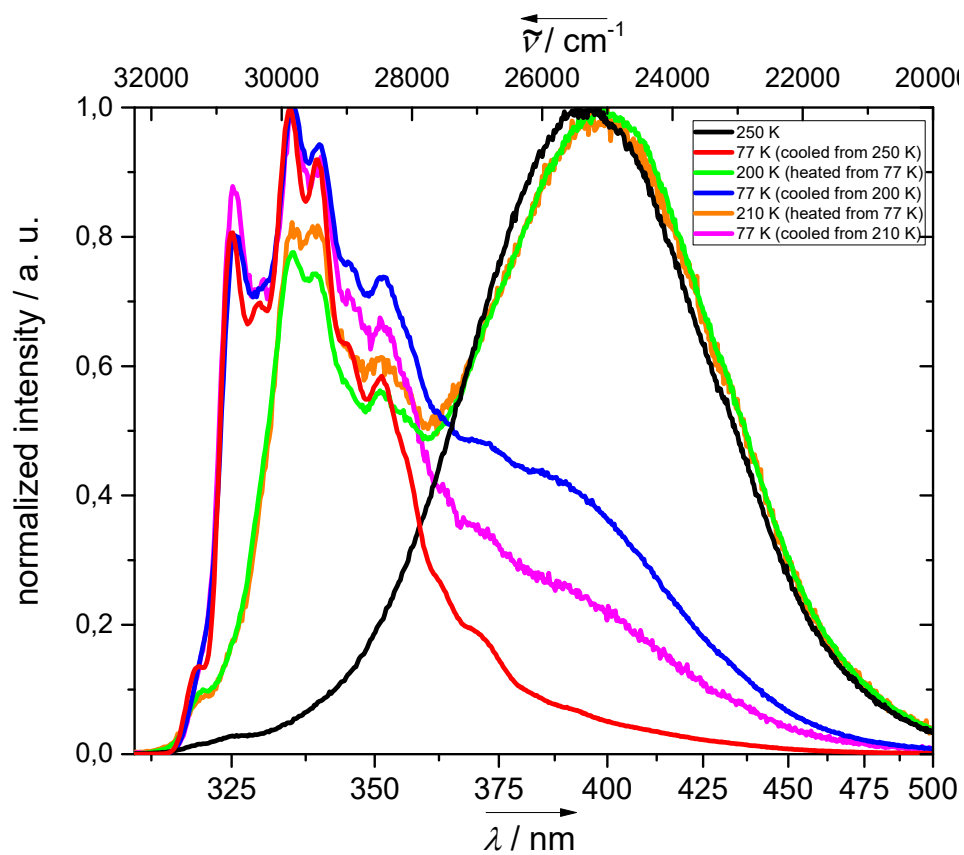


Figure S14. The normalized fluorescence emission spectra ($\lambda_{\text{exc}} = 274 \text{ nm}$) of the liquid MeNp at 250 K (black) and of the crystals at 77 K (cooled down from 250 K, red) heated to 200 K (green), cooled down to 77 K (blue), heated to 210 K (orange), and cooled down to 77 K (magenta).

S15 Emission spectra of the MeNp crystals at 190 K

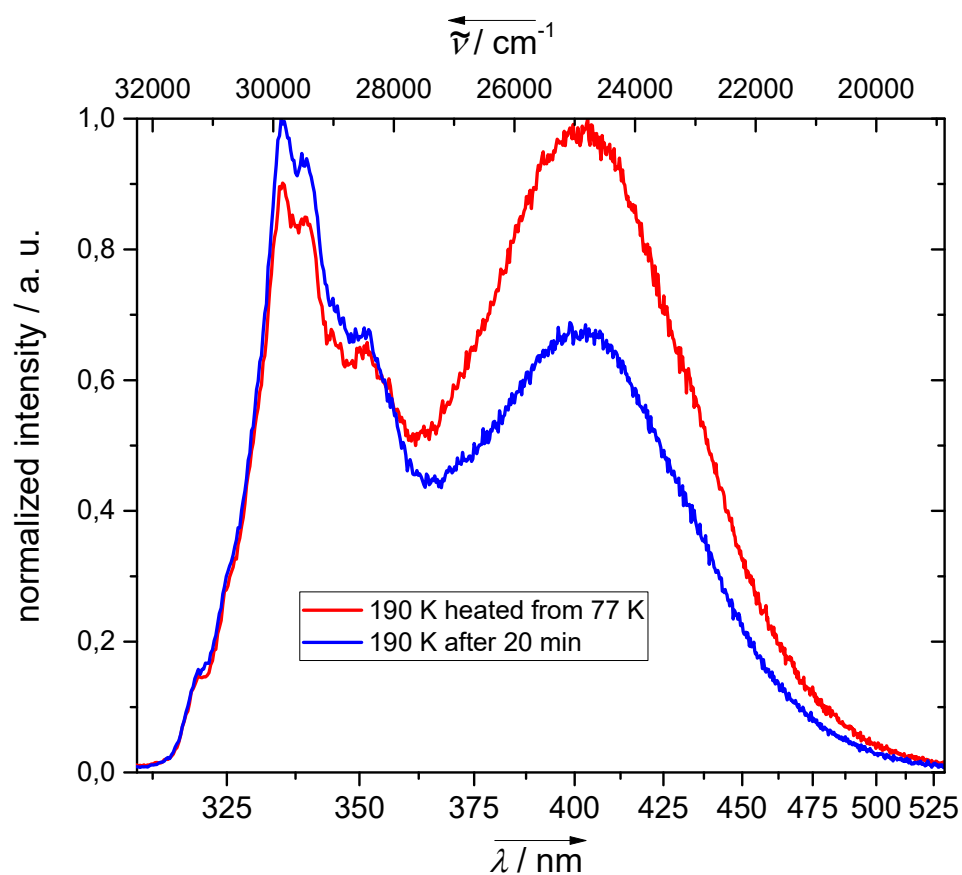


Figure S15. The normalized fluorescence emission spectra ($\lambda_{\text{exc}} = 274 \text{ nm}$) of the MeNp crystals heated from 77 K to 190 K (red) to be measured again at 190 K after 20 minutes (blue). The diminishing excimeric signal corresponds to the crystallization of the QLL.

Table S1 – Summary of the excitation (or absorption) maxima

Table S1. A summary of the excitation (or absorption) maxima. **A)** The maxima of the fluorescence excitation (or absorption) of the liquid MeNp at the indicated temperatures. * The fluorescence excitation ($\lambda_{\text{det}} = 350$ nm) of the 10^{-4} M MeNp solution in cyclohexane. ** The absorbance of the 10^{-4} M MeNp solution in cyclohexane. **B)** The maxima of the fluorescence excitation spectra of the MeNp crystals at the indicated temperatures. **C)** The maxima of the fluorescence excitation of the MeNp glass at the indicated temperatures. **D)** The spectrum of the MeNp dimer obtained through subtracting the excitation spectra.

	<i>T</i> / K	Excitation (or absorption) maxima λ / nm										
A) MeNp - liquid	295	250	257	265	278	291		302	307		324	332
	273	250	257	265	278	290		301	307		322	331
	255	250	257	265	278	290		301	307		322	331
A) MeNp in cyclohexane	295*	253		263	272	282	293			314	319	
A) MeNp in cyclohexane	295**			262	271	281	292			312	317	
B) MeNp - heating of crystals	77			265	273	285	296			312	317	321
	130			265	273	285	296			312	317	321
	150			265	273	285	296			312	317	322
	170			265	273	285	296			312	317	323
	180			265	273	285	296			312	317	323
	190			265	273	285	296			312	317	325
	200			265	273	285	296			312	317	326
	200 after 90 minutes			265	273	285	296			312	317	326
	205 - 215			265	273	285	296			312	317	326
C) MeNp - reheating of glass	77	250	259	267		281	292	302	307	312	318	324
	150	250	259	267		281	292	302	307	312	318	324
	160	251	260	268		281	292	302	306	312		324
	170	250	259	267		281	292	302	307	311	317	322
D) MeNp - dimer	200	250	258	266	277		291	300		313	318	

Table S2 – Summary of the emission maxima determined via numerical derivatives

Table S2. A summary of the emission maxima determined via numerical derivatives. **A)** The maxima of the fluorescence emission ($\lambda_{\text{exc}} = 274$ nm) of the slow-cooled MeNp. **B)** The maxima of the fluorescence emission ($\lambda_{\text{exc}} = 274$ nm) of the MeNp glass at 77 and 100 K.

	T / K	Emission maxima λ / nm																		
A) slow cooling of MeNp	273		323			337		352		366		383	387	391	395	404	407		419	435
	255	319	325		334	339	344	350	355	365	372	383	387	392	394	402	407		420	435
	215	318	324		334	339	347	352		363	372	383			395		406	413	419	435
	205	318	324		334	339	347	352		364	371	382		391		399	409		422	435
	190	318	324		333	339	347	351		364	371	383		391		400	408		420	434
	150	318	322	326	333	340	347	352		364	372	383		392		403	410		419	433
	77	318	325	329	334	338	345	352	356	363	372	383								
B) glass	77		325		331	339	343	351		362	369		387							
	100		325		332	339		351		362	372		389							

Table S3 – Maxima of the fluorescence emission of the MeNp glass

Table S3. The maxima of the excimer fluorescence emission of the MeNp glass ($\lambda_{\text{exc}} = 274$ nm) at the indicated temperatures, processed by applying numerical derivatives.

<i>T</i> / K	77	100	110	120	130	140	150	160	170	180
Emission maxima λ / nm	387	389	389	389	391	391	391	392	398	399

Table S4 – Bragg diffraction maxima of the MeNp

Table S4. The maxima of the X-ray diffractograms of the fast cooled MeNp from Figure S11 at the indicated temperatures.

<i>T</i> /K	2θ / °														
77	11.4	17.6	19.9		21.3	21.6	21.9	23		25	25.9	27.4	28.8	31	34.4
150	11.3	17.6	19.8		21.2	21.4		22.9		25	25.8	27.3	28.7	30.7	34.3
190	11.3	17.8	19.7		21			22.8			25.6	27.1	28.7	30.6	34.2
210	11.3	17.3	19.6	20.4	21.2			22.8	24.6	24.9	25.6	27.1	28.6	30.8	34
80	11.4	17.5	19.9	20.5	21.5			23		25.1	25.9	27.5	28.8	31	34.4