

## Supporting Information

### **Synthesis and optical properties of covalently bound Nile Red in mesoporous silica hybrids - Comparison of dye distribution of materials prepared by facile grafting and by co-condensation routes.**

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# 1. Structural characterization of grafted and cocondensed materials 6 and 7

## 1.1. Nitrogen sorption measurements

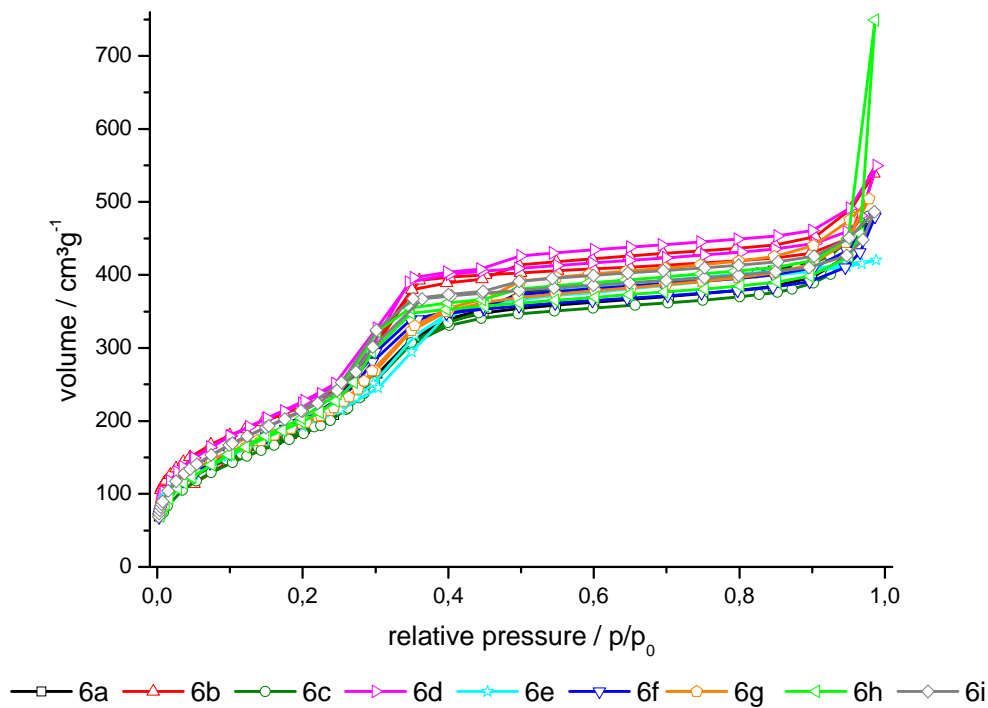


Figure S 1: Nitrogen sorption isotherms of grafted samples **6**. The deep adsorption increase of hybrid **6h** at relative pressures close to the saturation pressure is attributed to nitrogen condensation in interparticle voids.

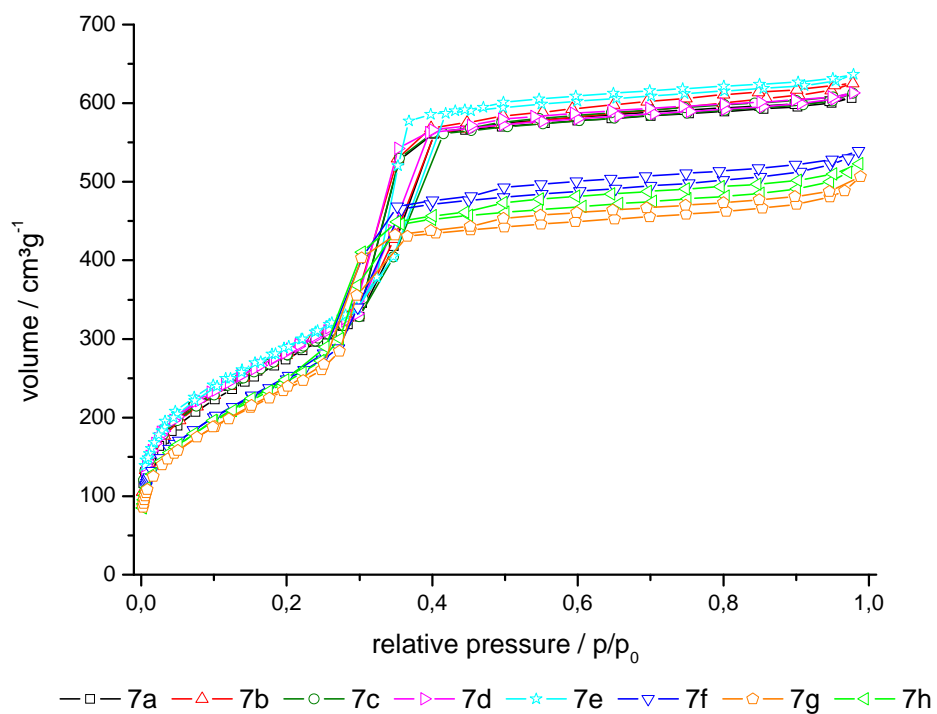


Figure S 2: Nitrogen sorption isotherms of co-condensed samples **7**.

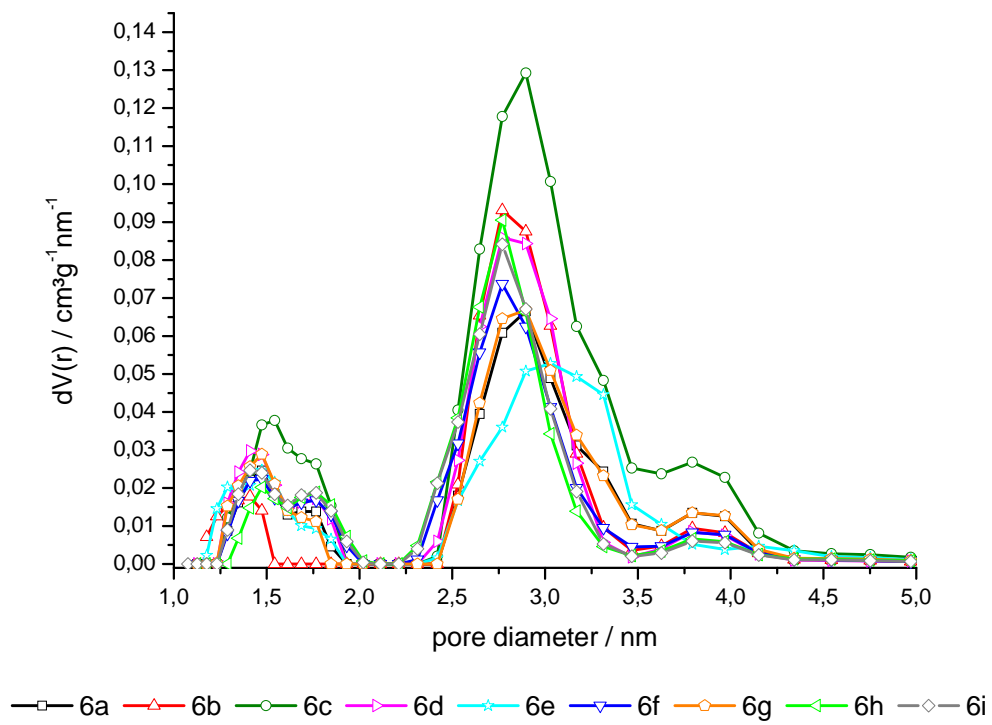


Figure S 3: pore size distribution curves of grafted samples **6**.

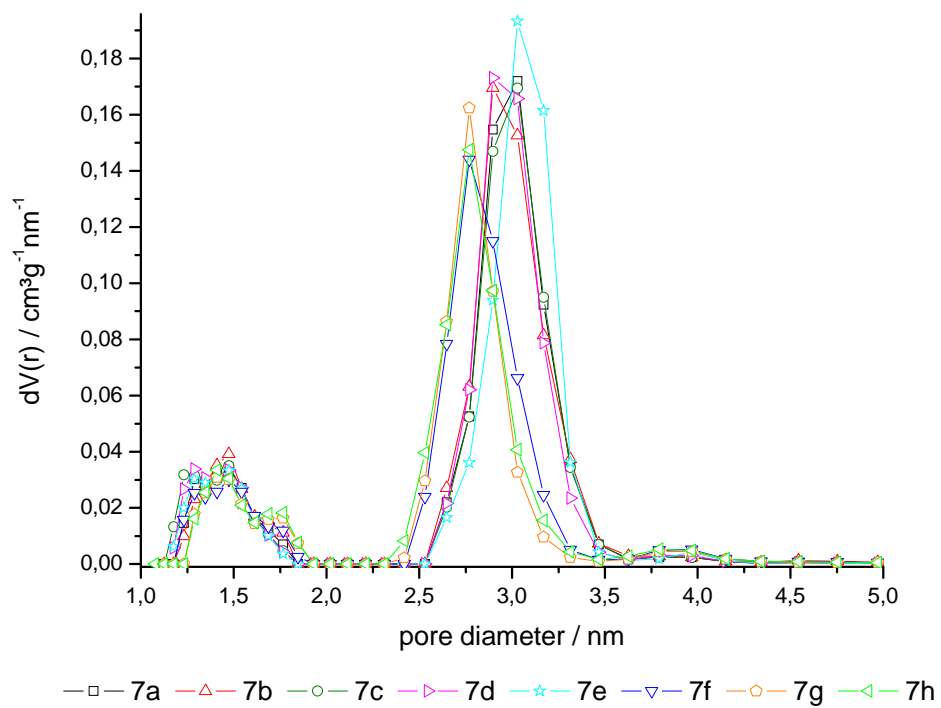


Figure S 4: pore size distribution curves of co-condensed samples **7**.

1.2. Small angle x-ray scattering (SAXS)

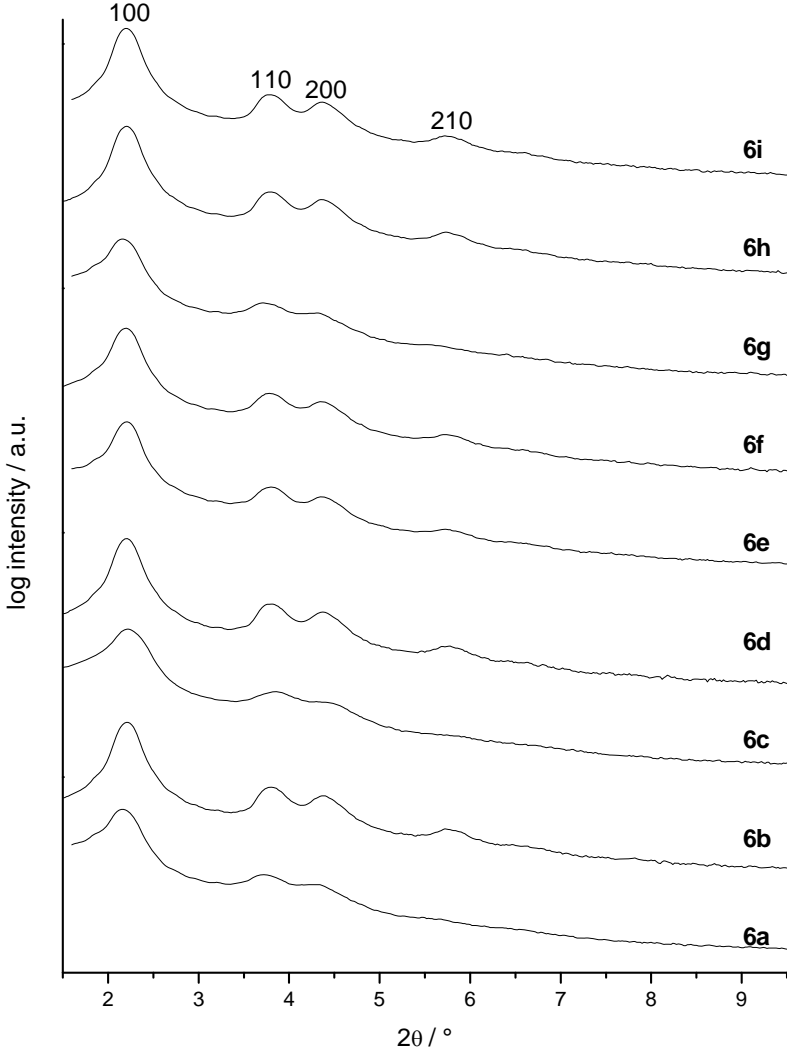


Figure S 5: SAXS pattern of grafted samples 6.

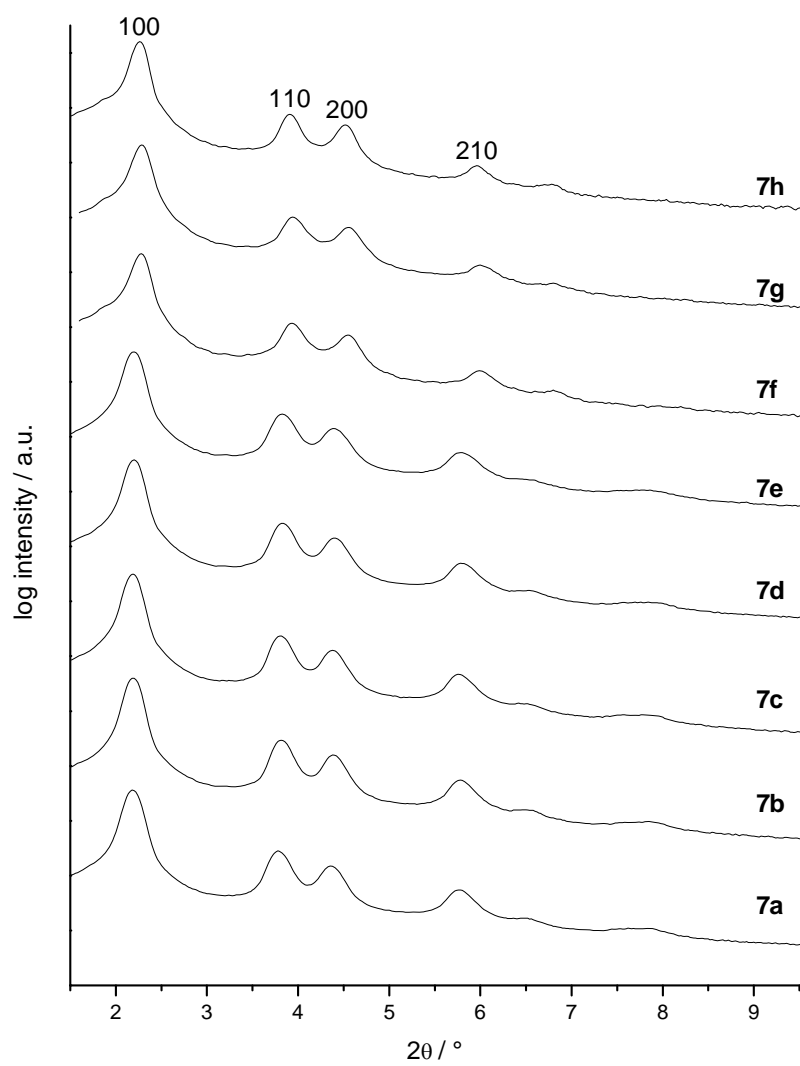


Figure S 6: SAXS pattern of co-condensed samples 7.

### 1.3. Transmission electron microscopy (TEM)

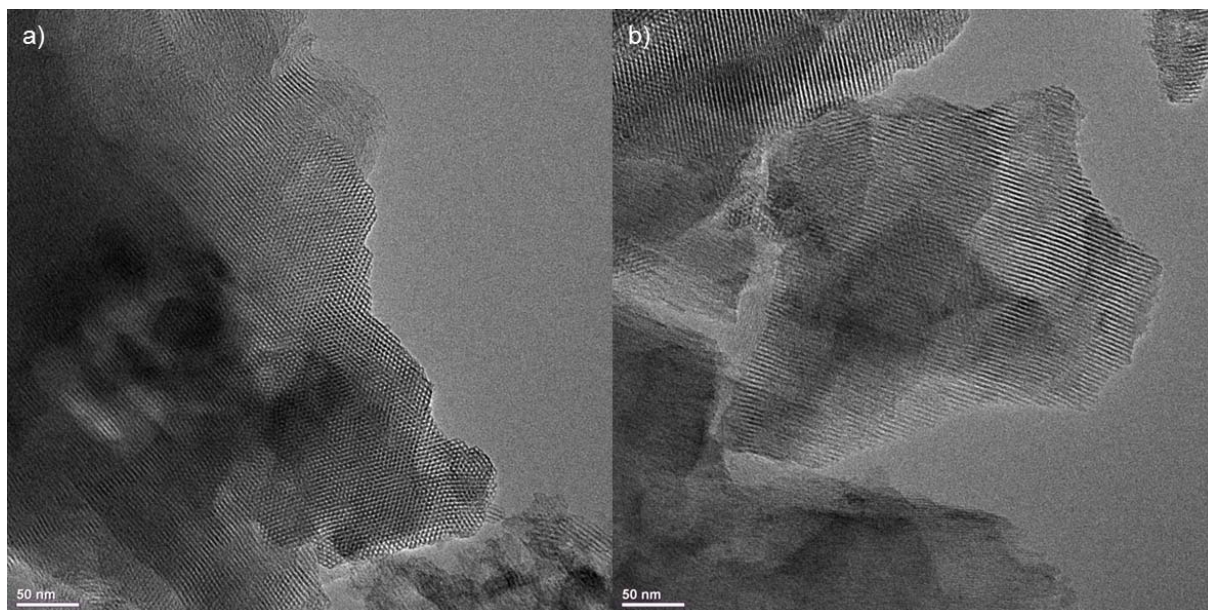


Figure S 7: TEM images of **6a** a) along the channel direction and b) perpendicular to the channel direction.

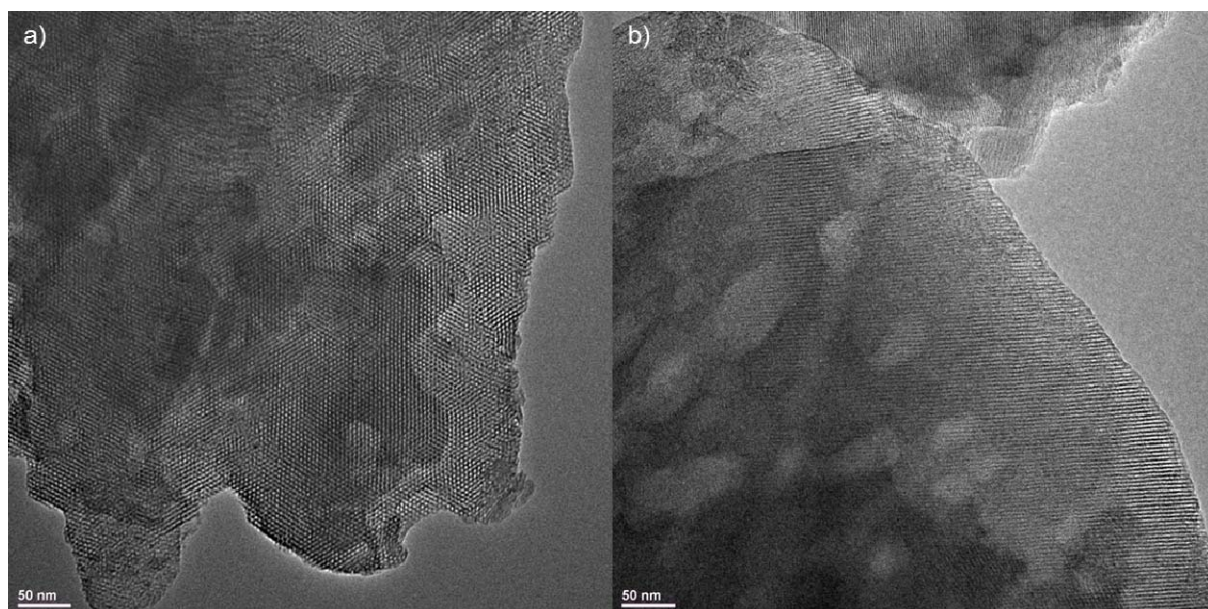


Figure S 8: : TEM images of **6b** a) along the channel direction and b) perpendicular to the channel direction.

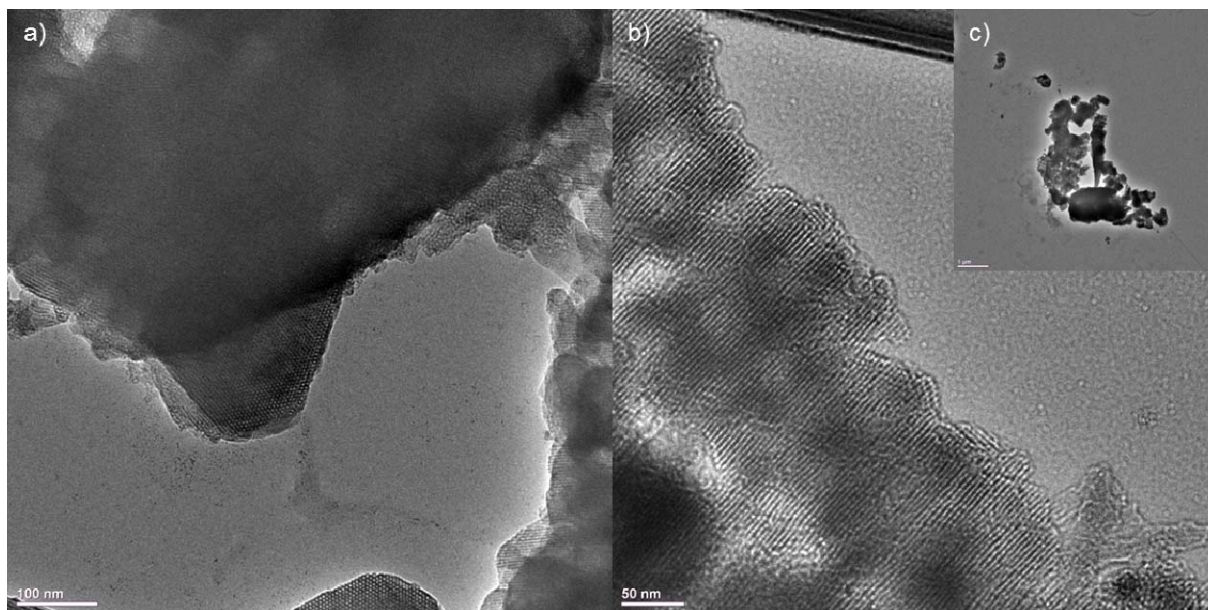


Figure S 9: TEM images of **6c** a) along the channel direction, b) perpendicular to the channel direction and c) large scale.

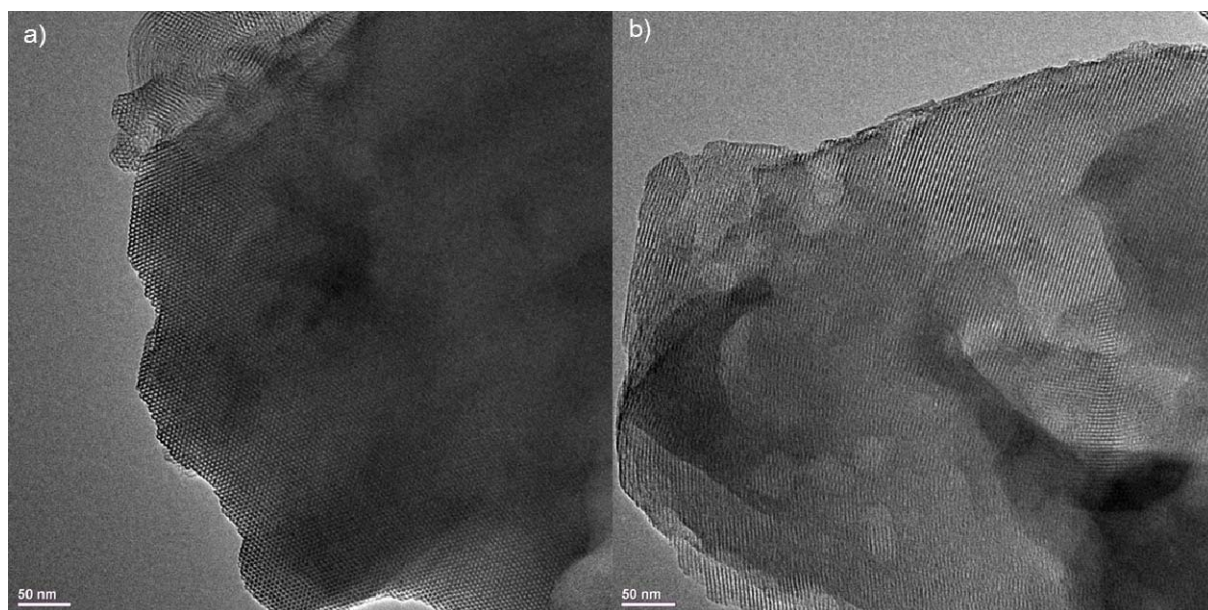


Figure S 10: TEM images of **6d** a) along the channel direction and b) perpendicular to the channel direction.

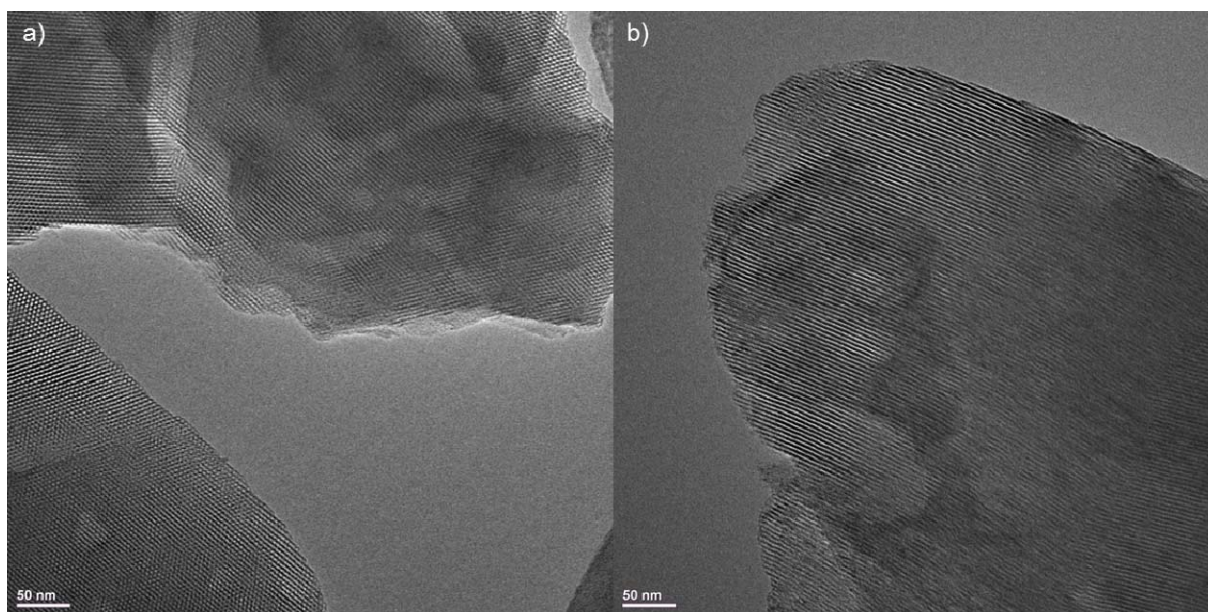


Figure S 11: TEM images of **6e** a) along the channel direction and b) perpendicular to the channel direction.

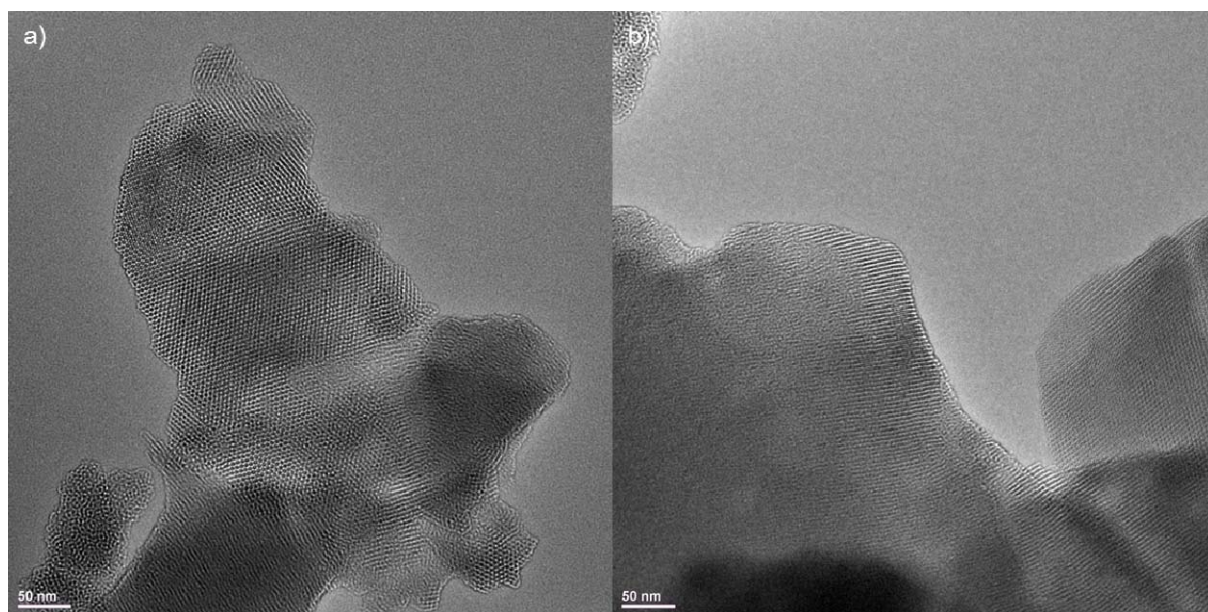


Figure S 12: TEM images of **6f** a) along the channel direction and b) perpendicular to the channel direction.



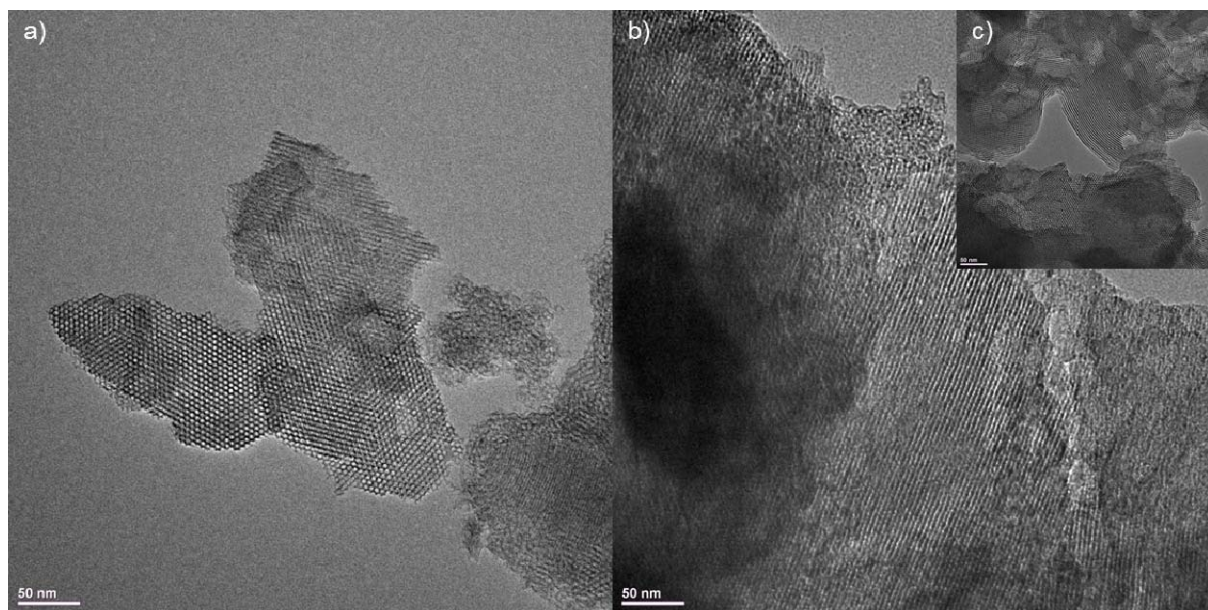


Figure S 13: TEM images of **6g** a) along the channel direction, b) perpendicular to the channel direction and c) mixed phase.

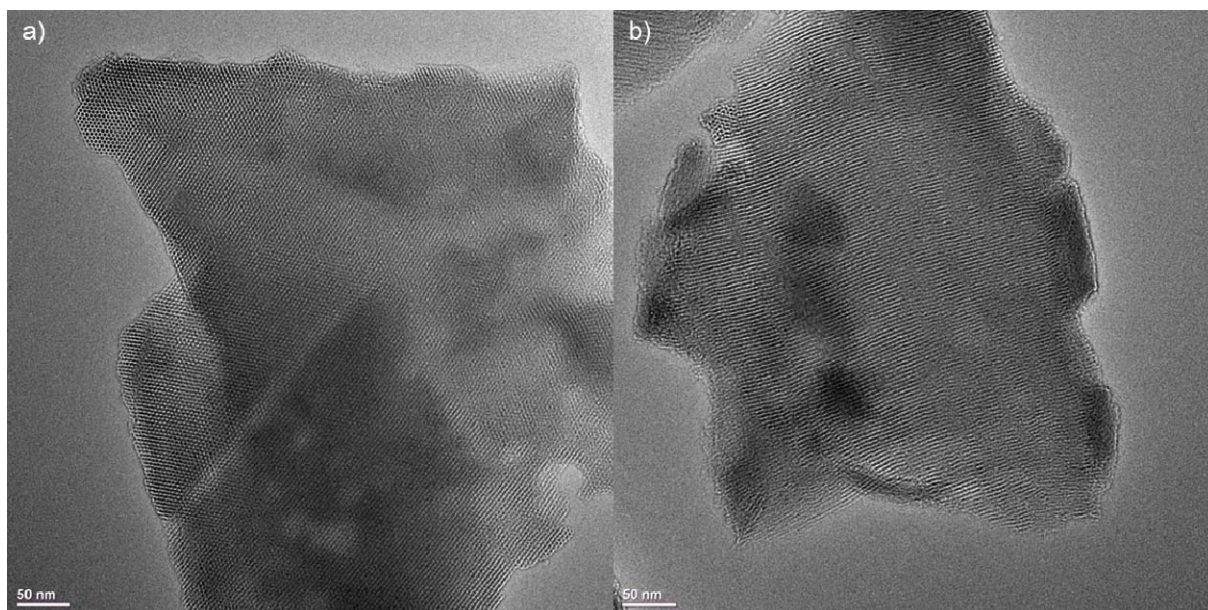


Figure S 14: TEM images of **6h** a) along the channel direction and b) perpendicular to the channel direction.

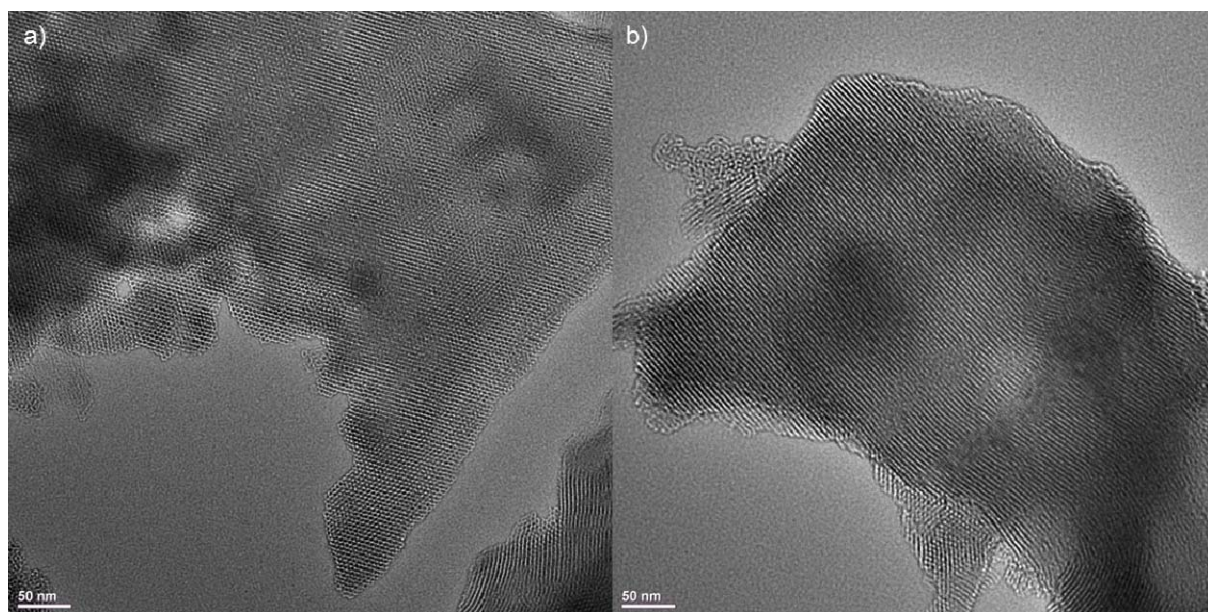


Figure S 15: TEM images of **6i** a) along the channel direction and b) perpendicular to the channel direction.

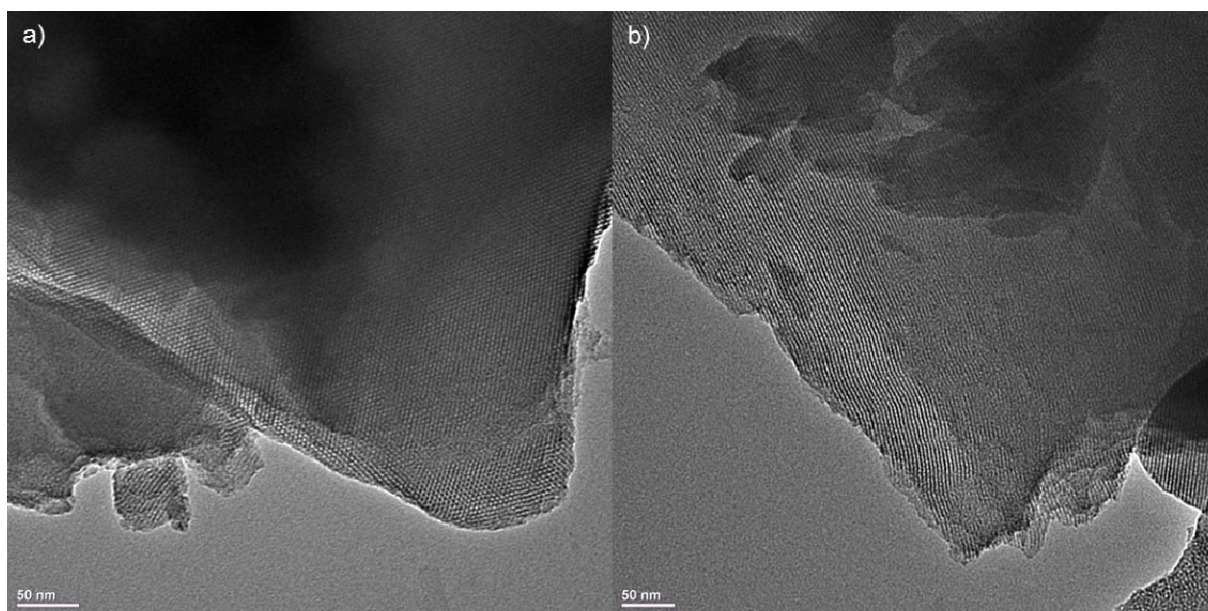


Figure S 16: TEM images of **7a** a) along the channel direction and b) perpendicular to the channel direction.

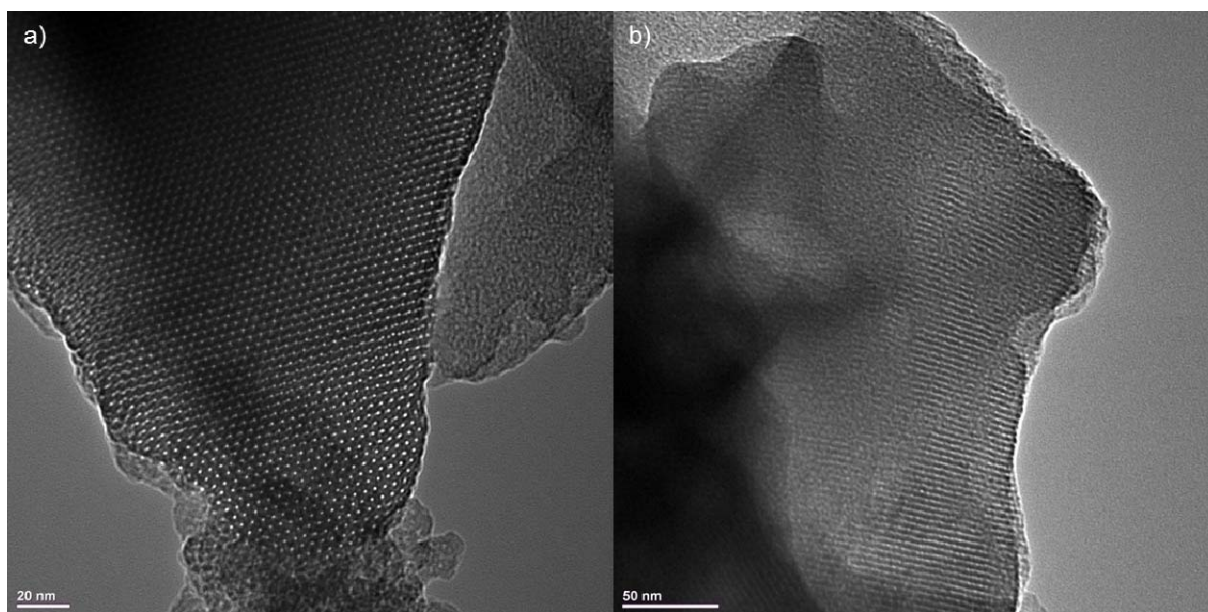


Figure S 17: TEM images of **7b** a) along the channel direction and b) perpendicular to the channel direction.

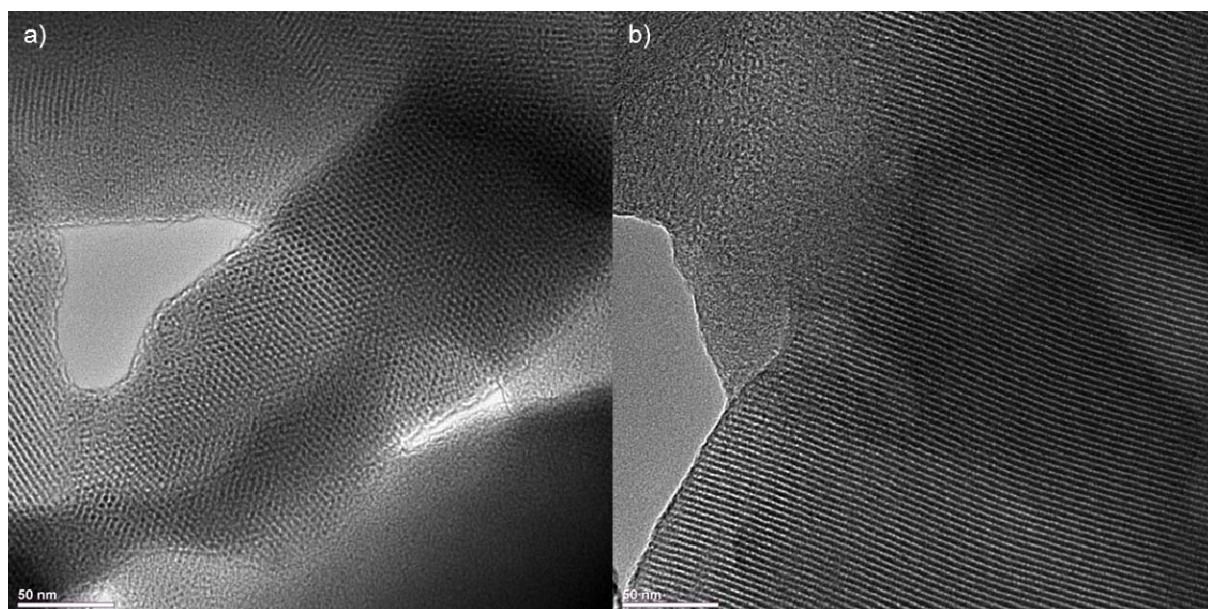


Figure S 18: TEM images of **7c** a) along the channel direction and b) perpendicular to the channel direction.

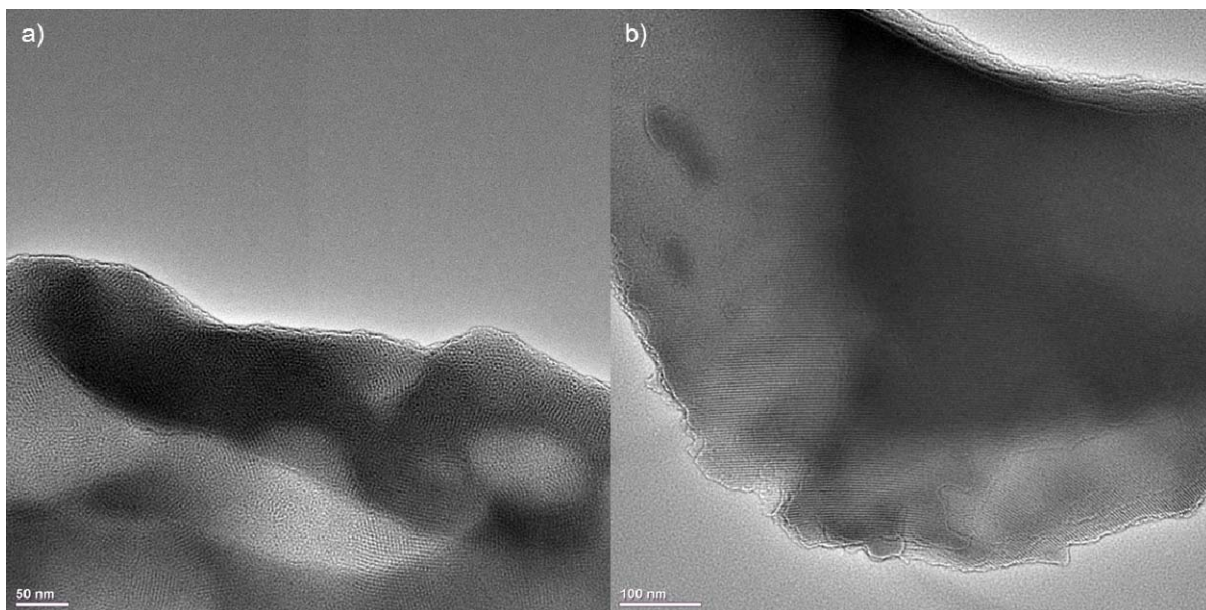


Figure S 19: TEM images of **7d** a) along the channel direction and b) perpendicular to the channel direction.

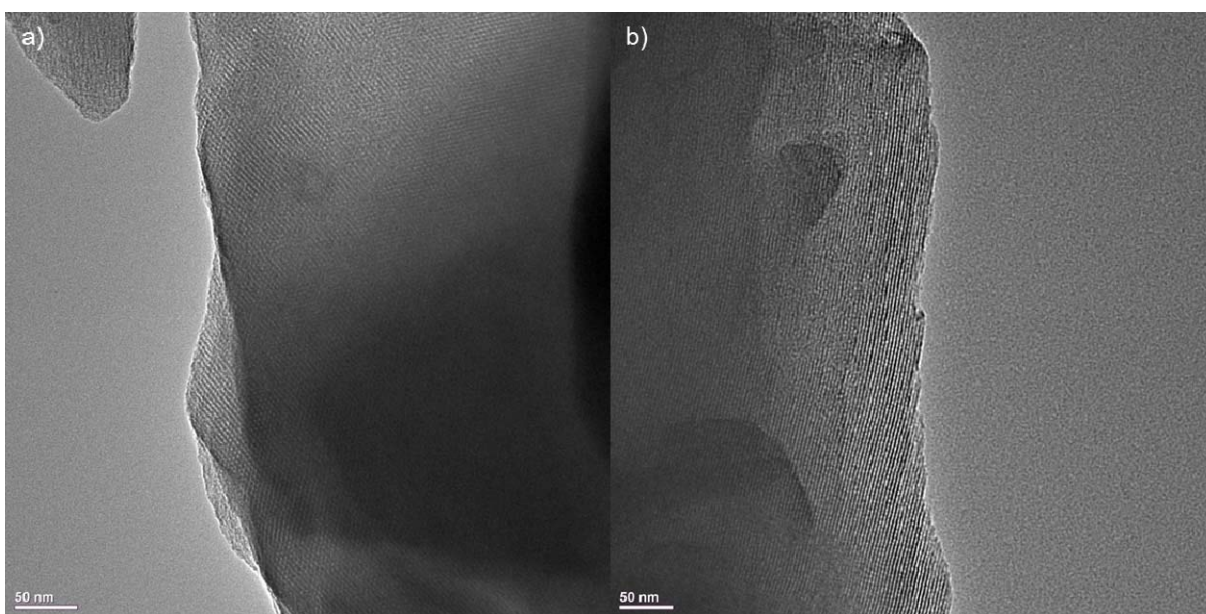


Figure S 20: TEM images of **7e** a) along the channel direction and b) perpendicular to the channel direction.

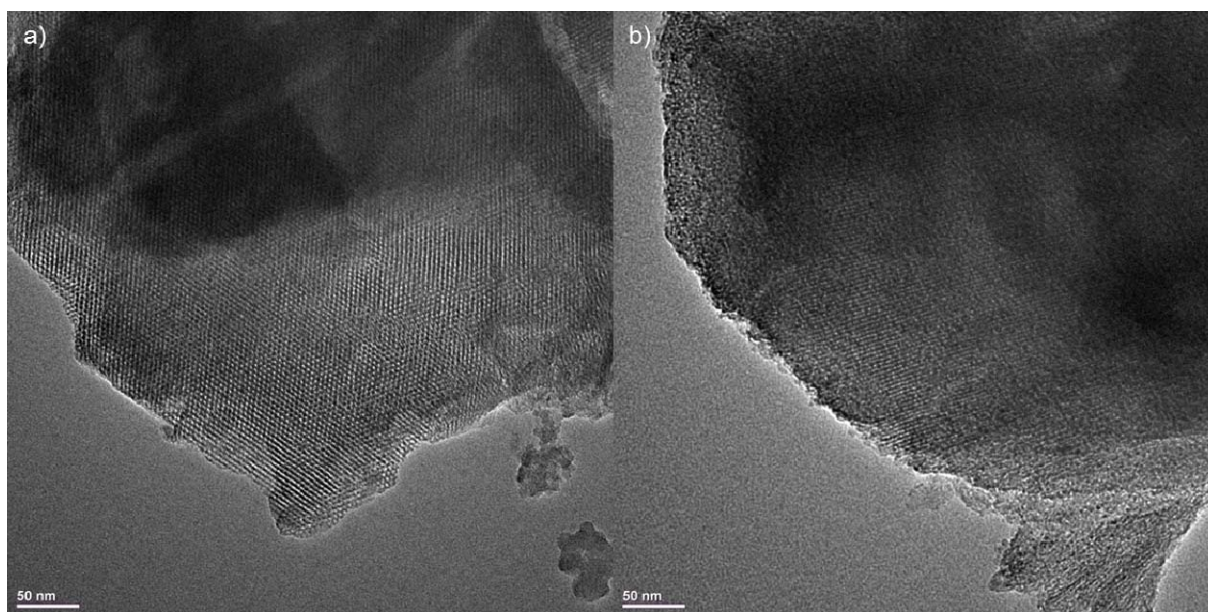


Figure S 21: TEM images of **7f** a) along the channel direction and b) perpendicular to the channel direction.

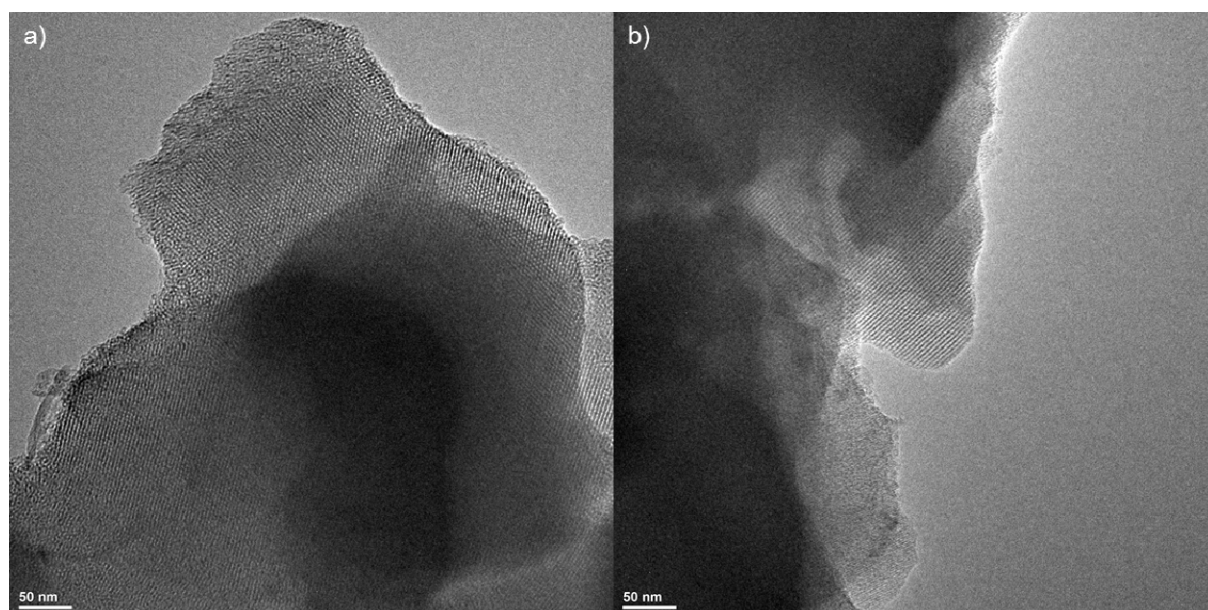


Figure S 22: TEM images of **7g** a) along the channel direction and b) perpendicular to the channel direction.

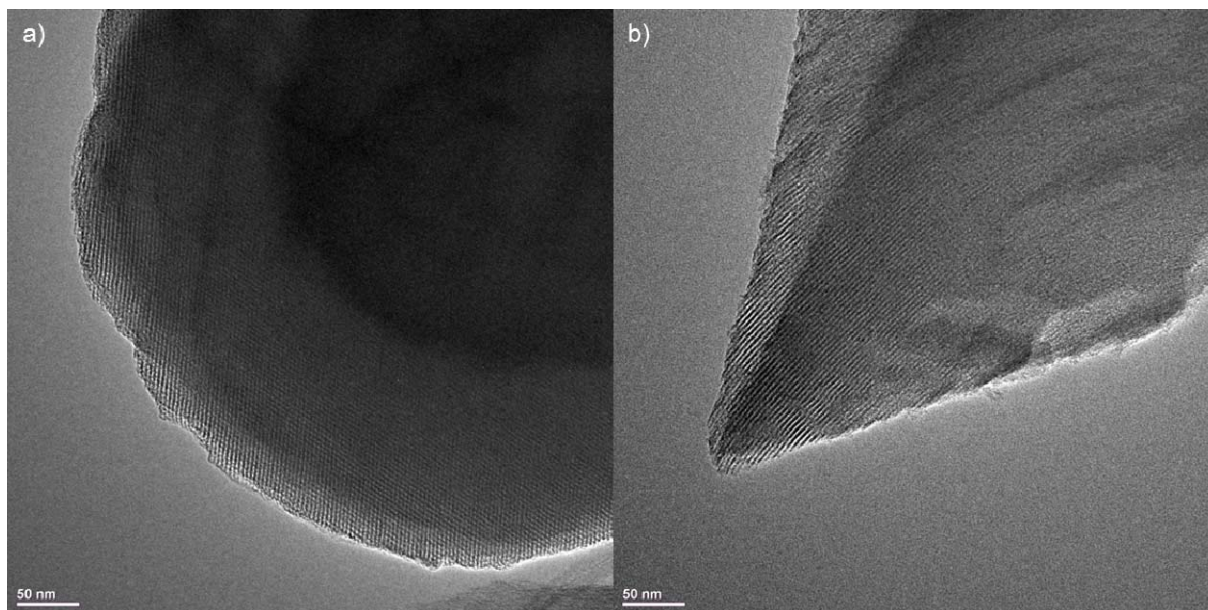


Figure S 23: TEM images of **7h** a) along the channel direction and b) perpendicular to the channel direction.

## 2. Spectroscopic properties of precursor **5**, and hybrid materials **6** and **7**

### 2.1. Solvatochromism of precursor **5**

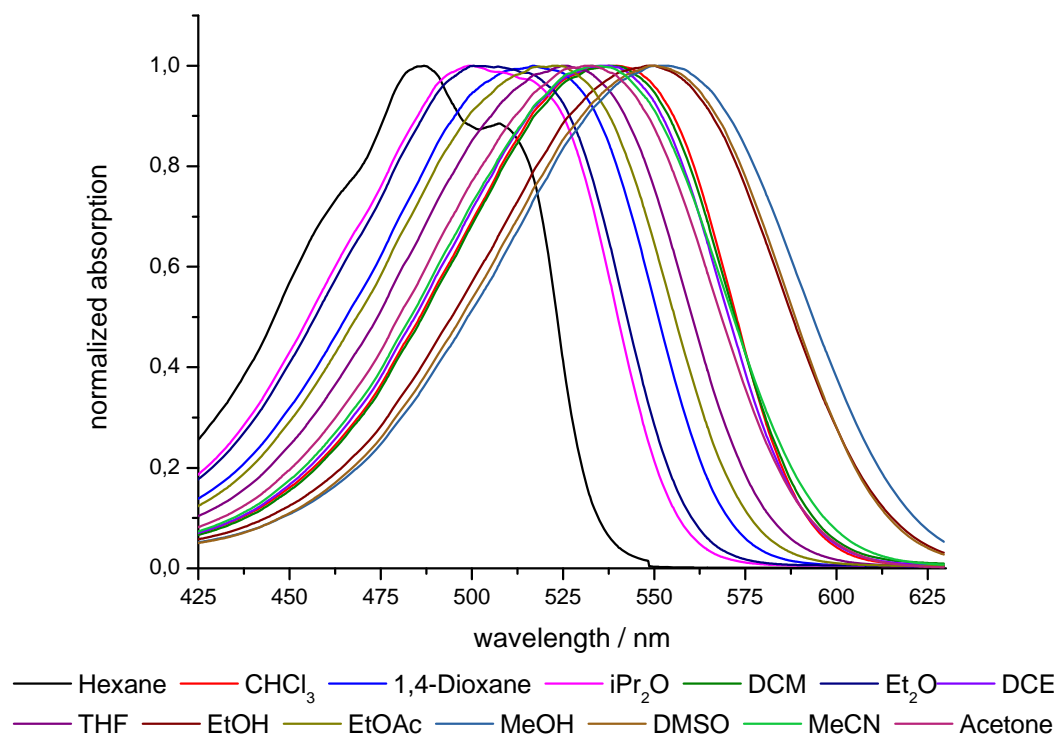


Figure S 24: Absorption spectra of **5** in different solvents.

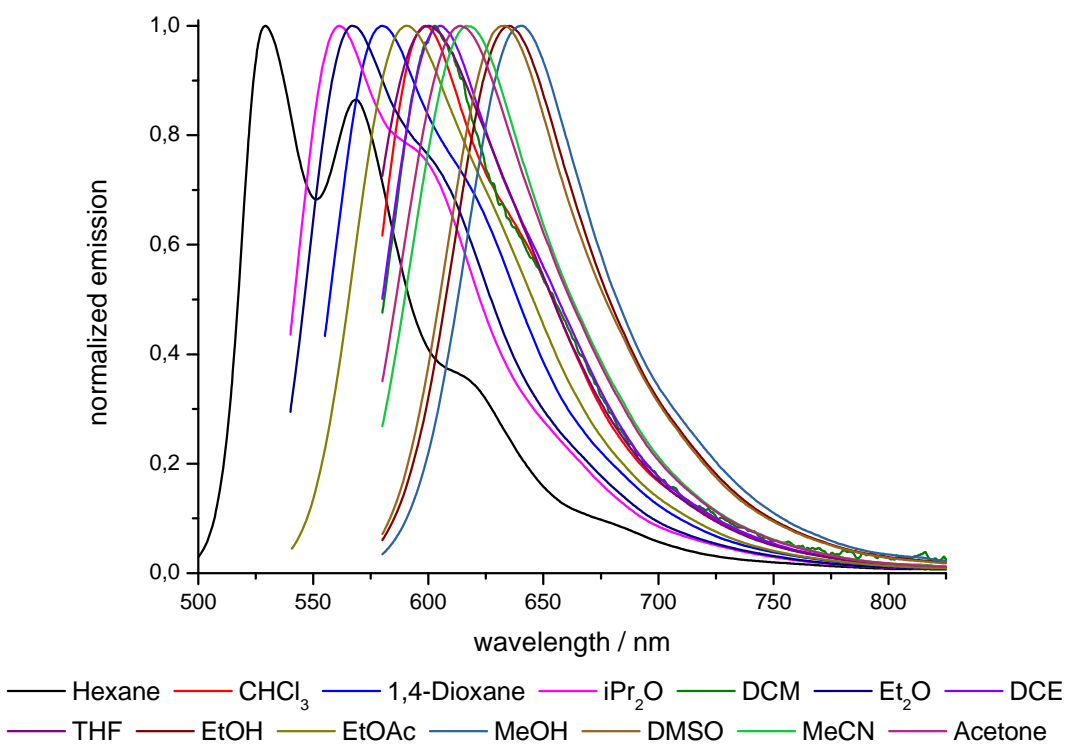


Figure S 25: Emission spectra of **5** in different solvents.

The molar extinction coefficient of precursor **5** in DMSO was determined to be  $\epsilon_{539\text{nm}} = 21000 \text{ M}^{-1}\text{cm}^{-1}$ .

## 2.2. Determination of dye concentration inside materials 6 and 7

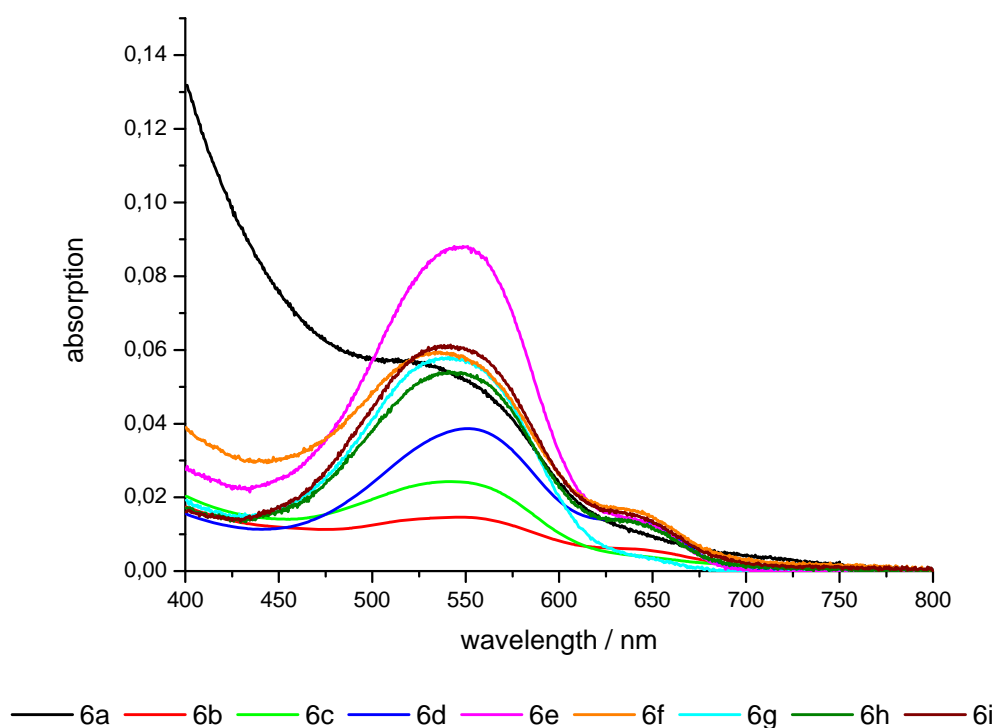


Figure S 26: UV/Vis-spectra of grafted hybrid materials suspended in DMSO with  $c(\mathbf{6a}) = 3.0$  g/L,  $c(\mathbf{6b-6g}) = 0.3$  g/L,  $c(\mathbf{6h}) = 0.15$  g/L,  $c(\mathbf{6i}) = 0.12$  g/L.

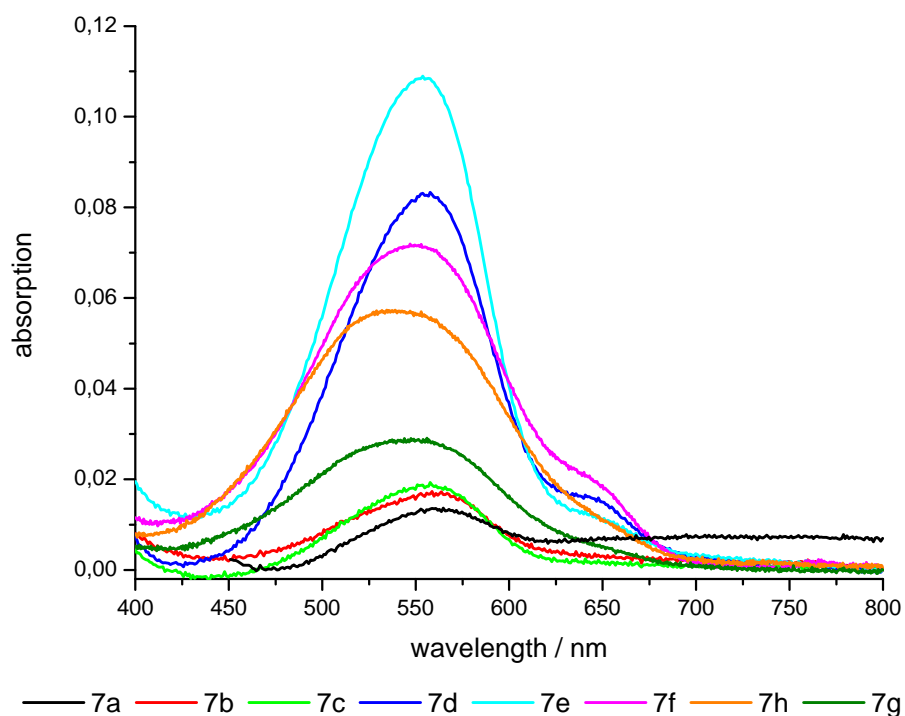


Figure S 27: UV/Vis-spectra of co-condensed hybrid materials suspended in DMSO with  $c(\mathbf{7a}) = 10$  g/L,  $c(\mathbf{7b-7e}) = 3.0$  g/L,  $c(\mathbf{7f}) = 0.30$  g/L,  $c(\mathbf{7g}) = 0.075$  g/L,  $c(\mathbf{7h}) = 0.060$  g/L.



### 2.3. Solvatochromism of hybrid materials **6** and **7**

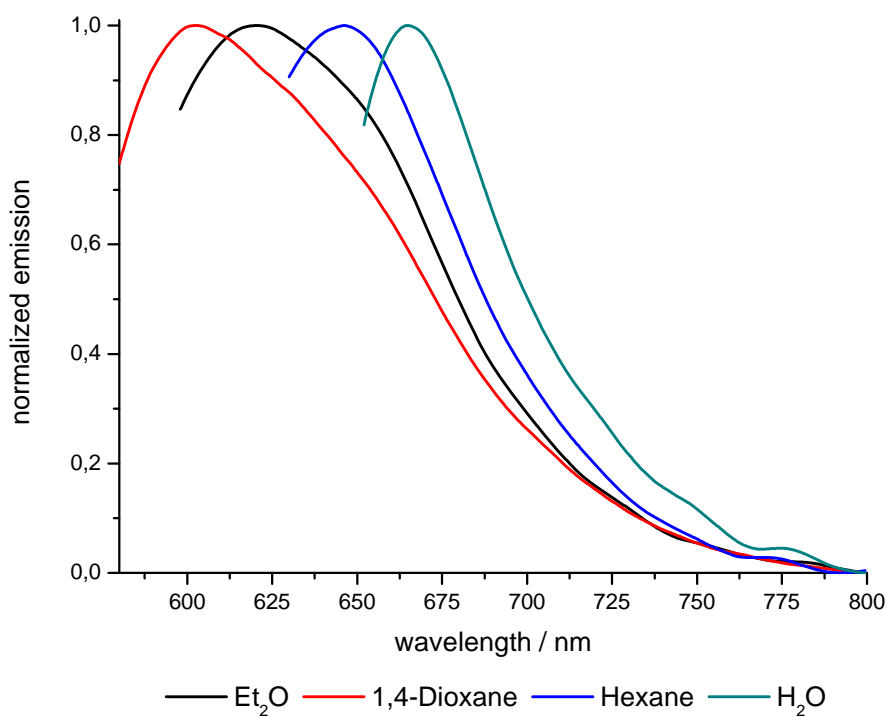


Figure S 28: normalized emission spectra of **6b** in different solvents.

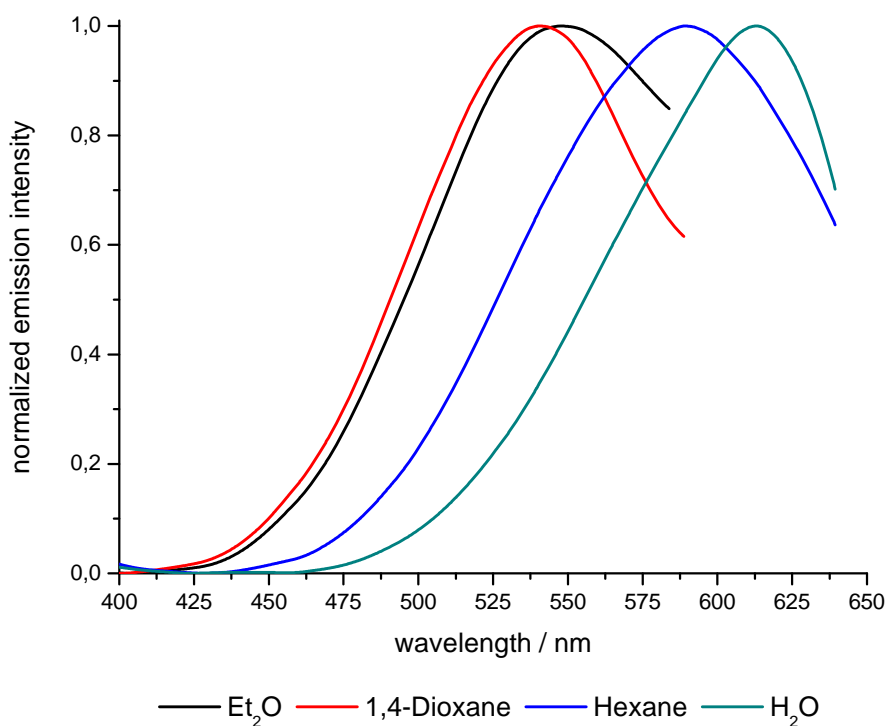


Figure S 29: normalized excitation spectra of **6b** in different solvents ( $\lambda_{\text{emission}} = 660 \text{ nm}$ ).

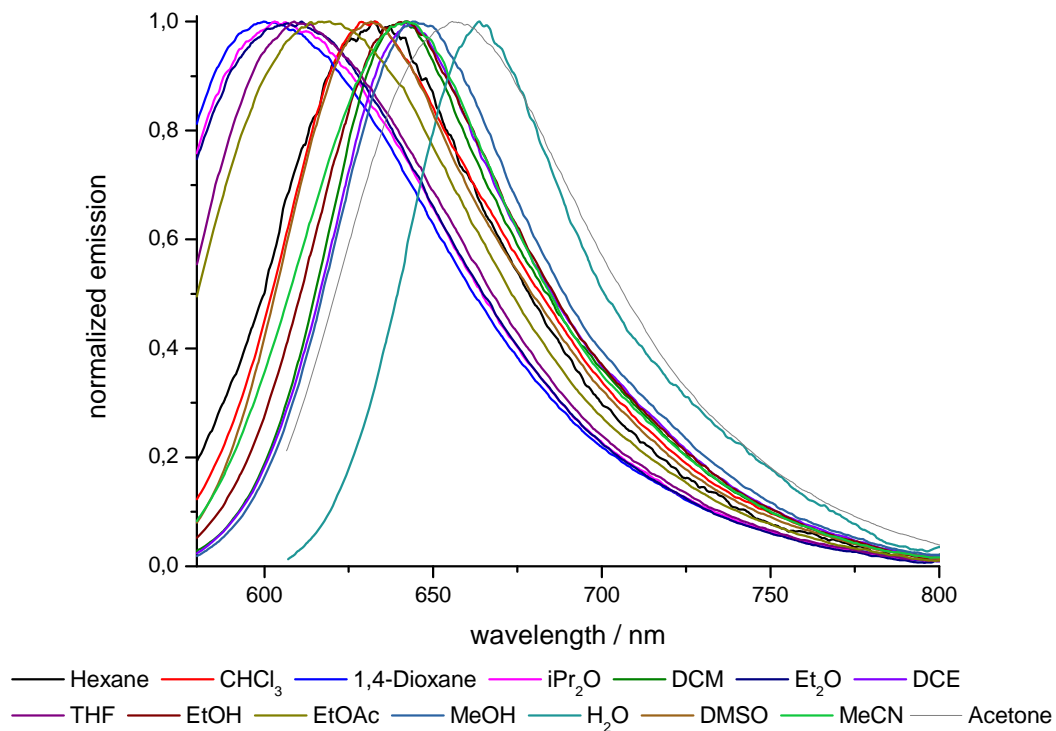


Figure S 30: normalized emission spectra of **7e** in different solvents.

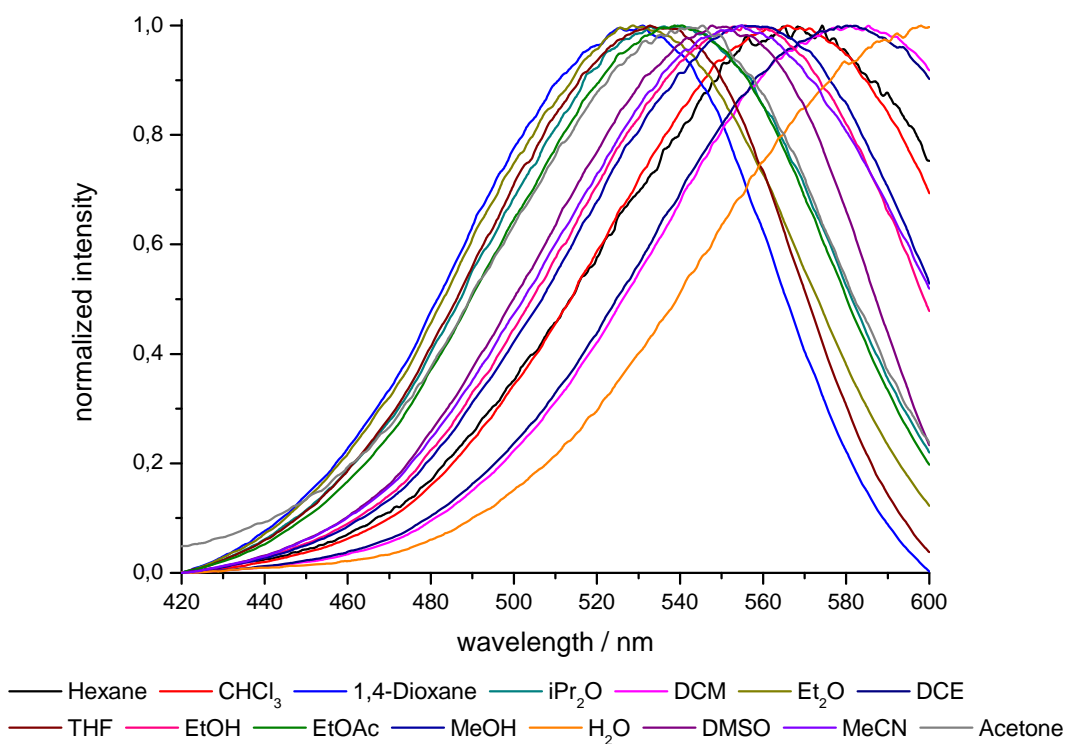


Figure S 31: normalized excitation spectra of **7e** in different solvents ( $\lambda_{\text{emission}} = 650 \text{ nm}$ ).

## 2.4. Excitation and emission spectra of hybrid materials 6 and 7 in the solid state

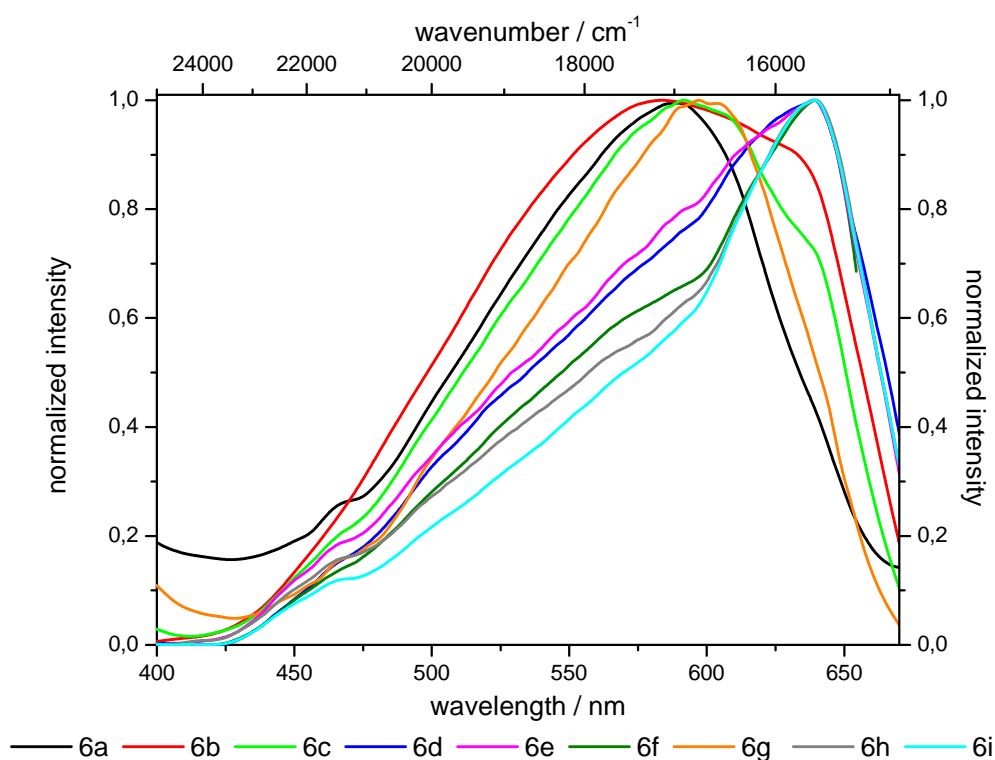


Figure S 32: normalized excitation spectra of grafted hybrid materials **6** (λ<sub>emission</sub> = 700 nm).

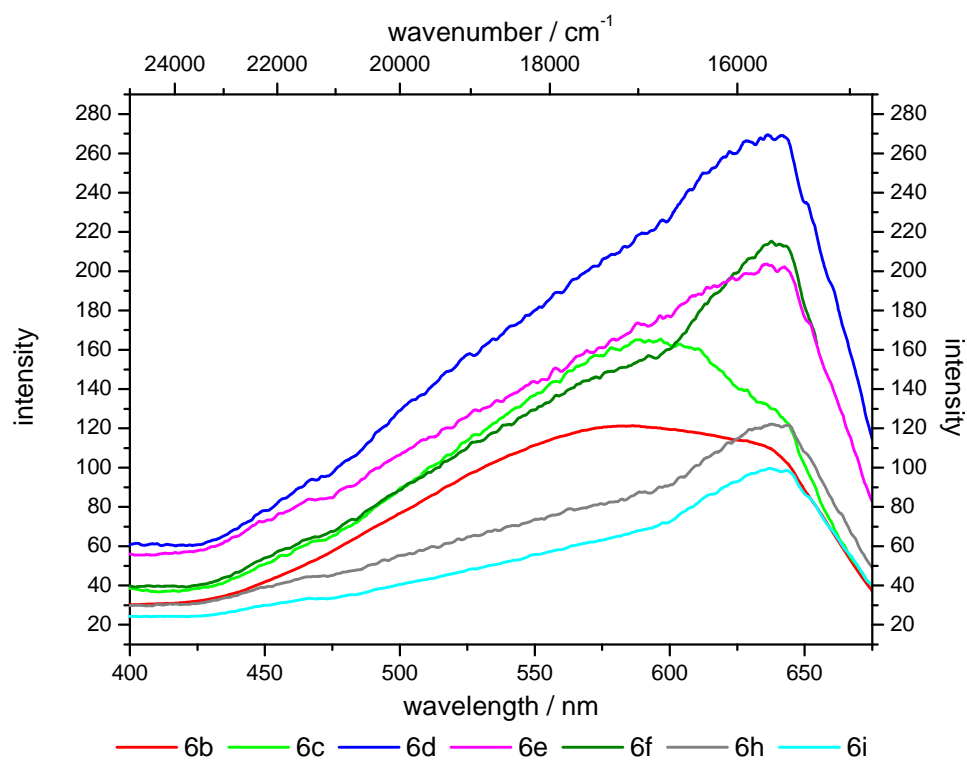


Figure S 33: excitation spectra of grafted hybrid materials **6** (λ<sub>emission</sub> = 700 nm). (Hybrid materials **6a** and **6g** not shown as they were measured in another setup.)

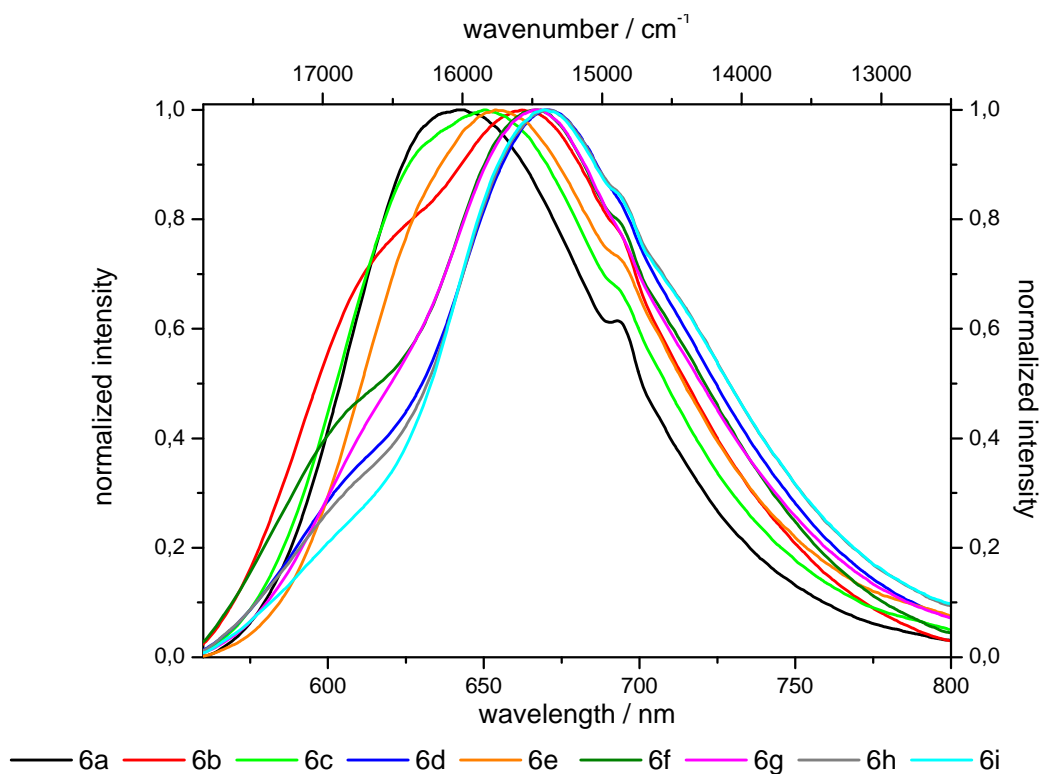


Figure S 34: normalized emission spectra of grafted hybrid materials **6**.

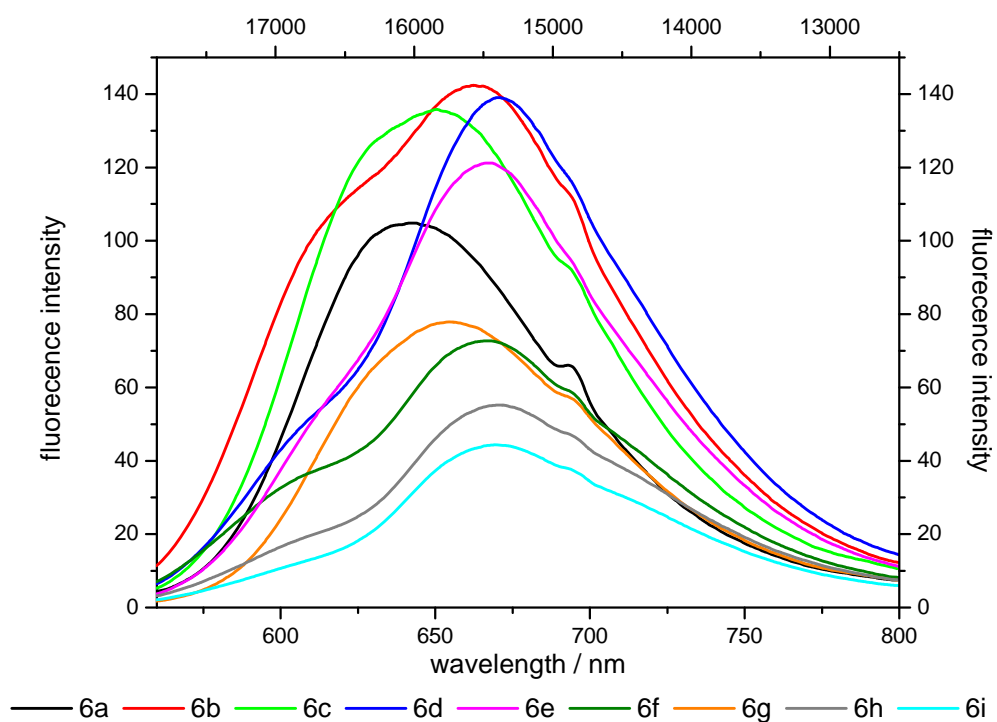


Figure S 35: emission spectra of grafted hybrid materials **6**.

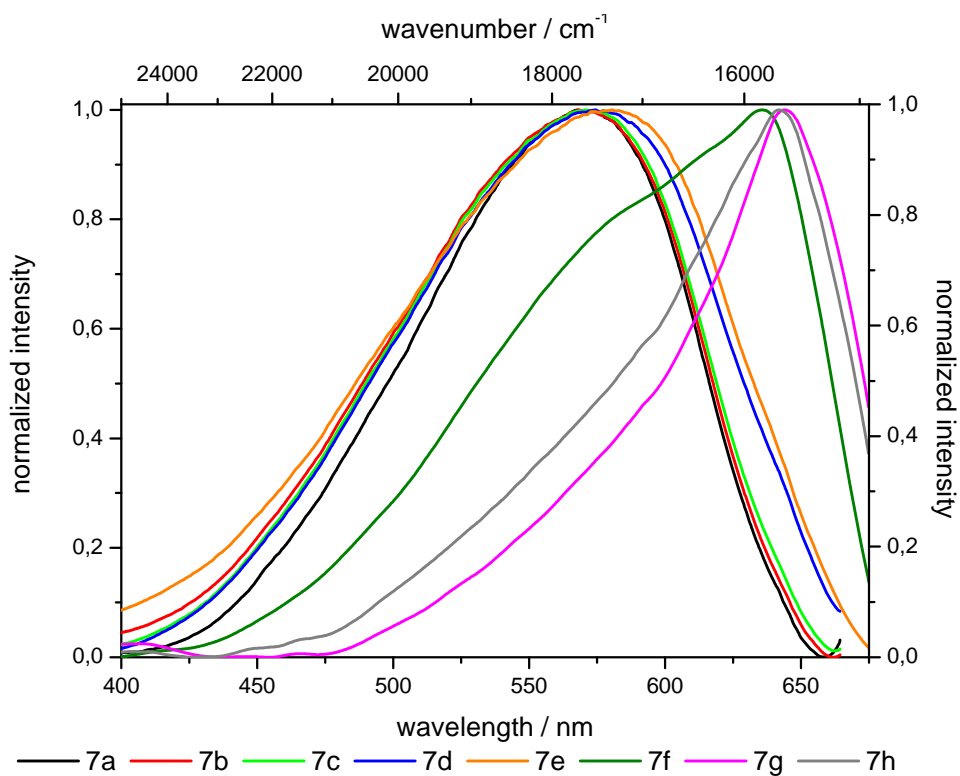


Figure S 36: normalized excitation spectra of co-condensed hybrid materials **7** ( $\lambda_{\text{emission}} = 700 \text{ nm}$ ).

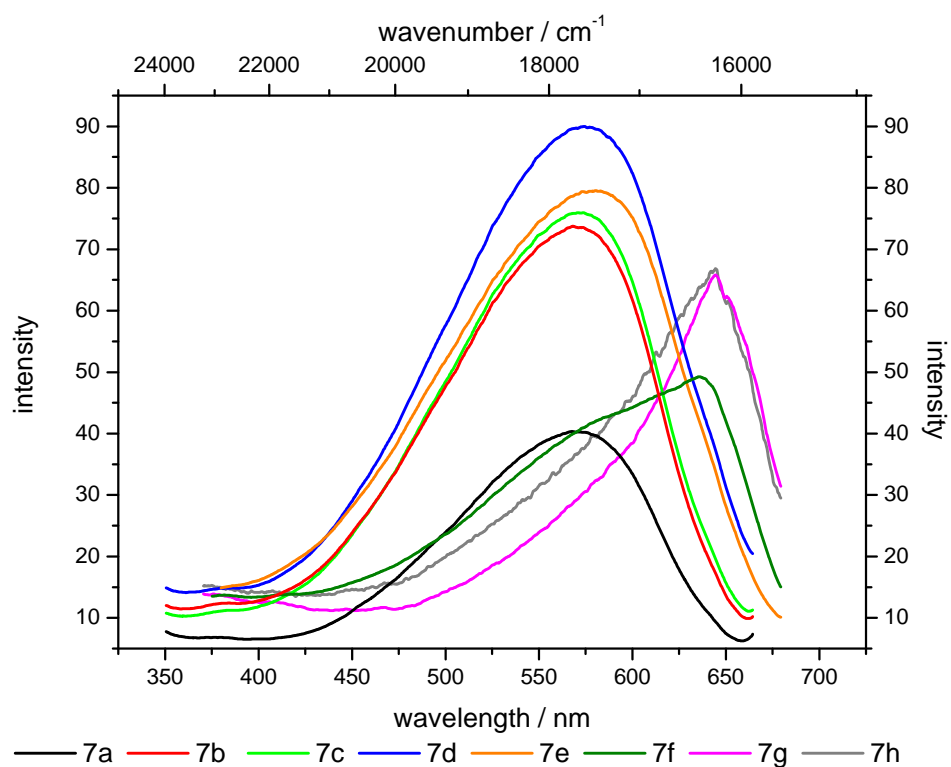


Figure S 37: excitation spectra of co-condensed hybrid materials **7** ( $\lambda_{\text{emission}} = 700 \text{ nm}$ ).

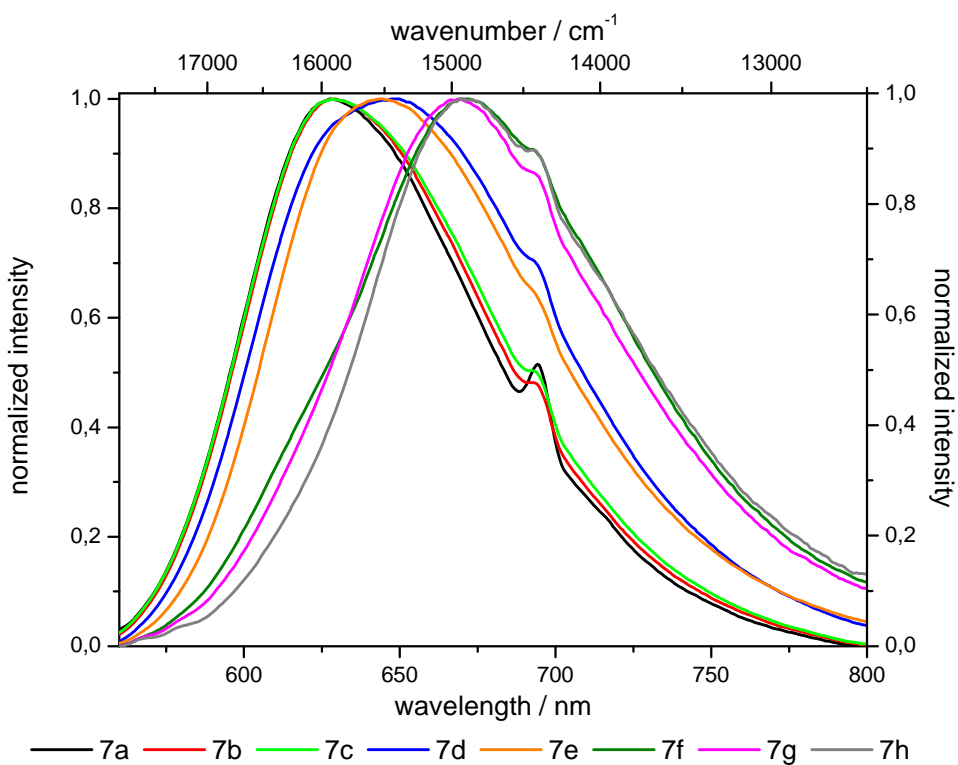


Figure S 38: normalized emission spectra of co-condensed hybrid materials **7**.

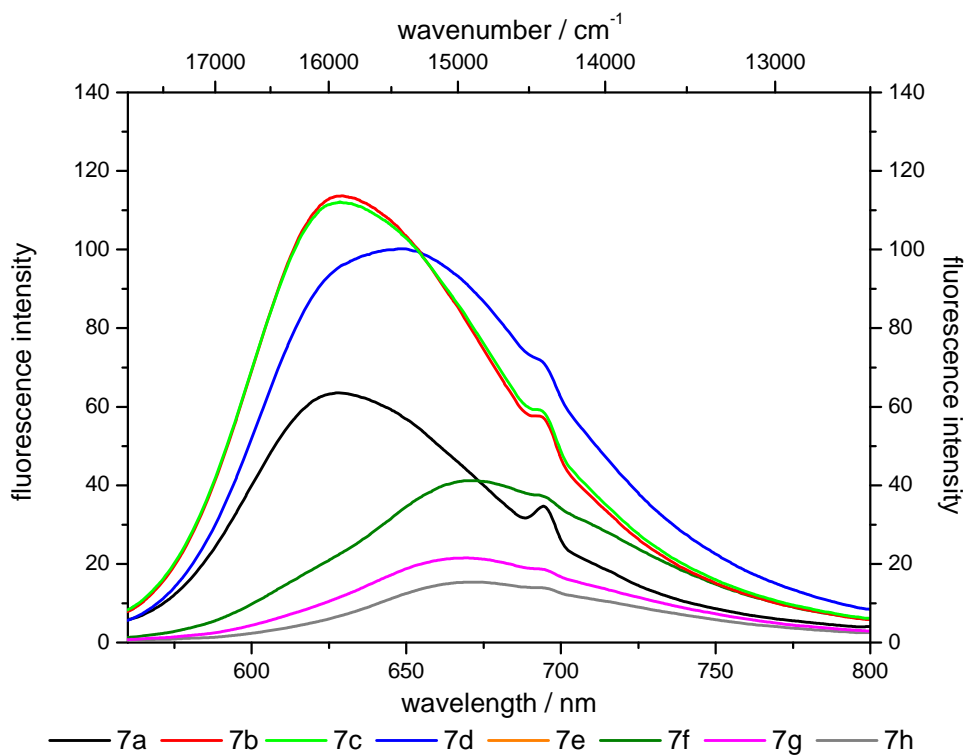


Figure S 39: emission spectra of co-condensed hybrid materials **7**.

## 2.5. Red-edge excitation shift (REES) of hybrid materials 6b and 7e

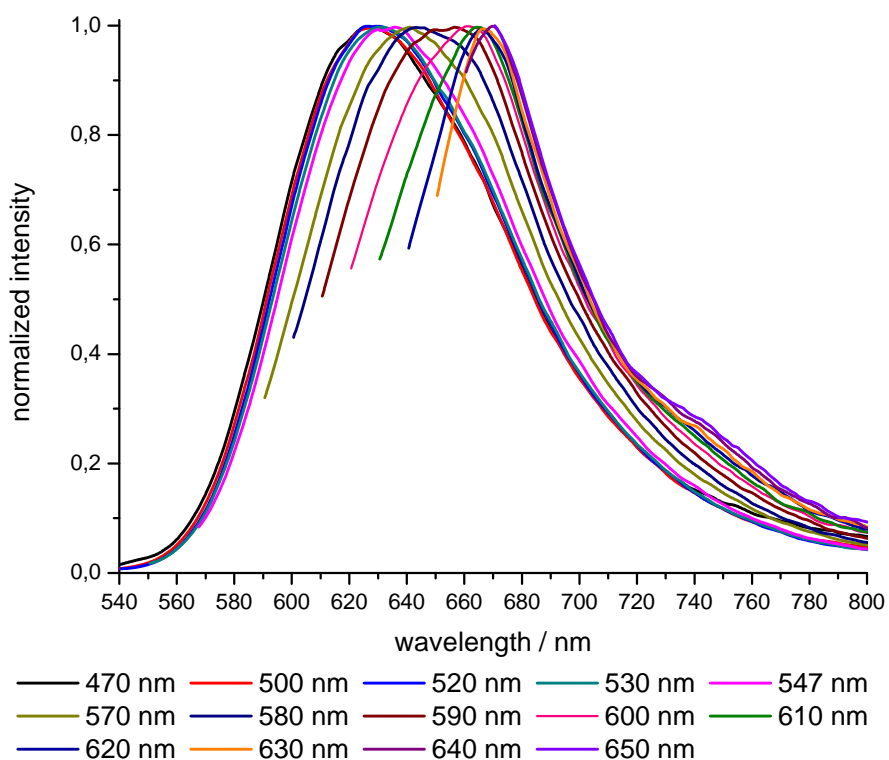


Figure S 40: Fluorescence spectra of **6b** at designated excitation wavelengths showing REES.

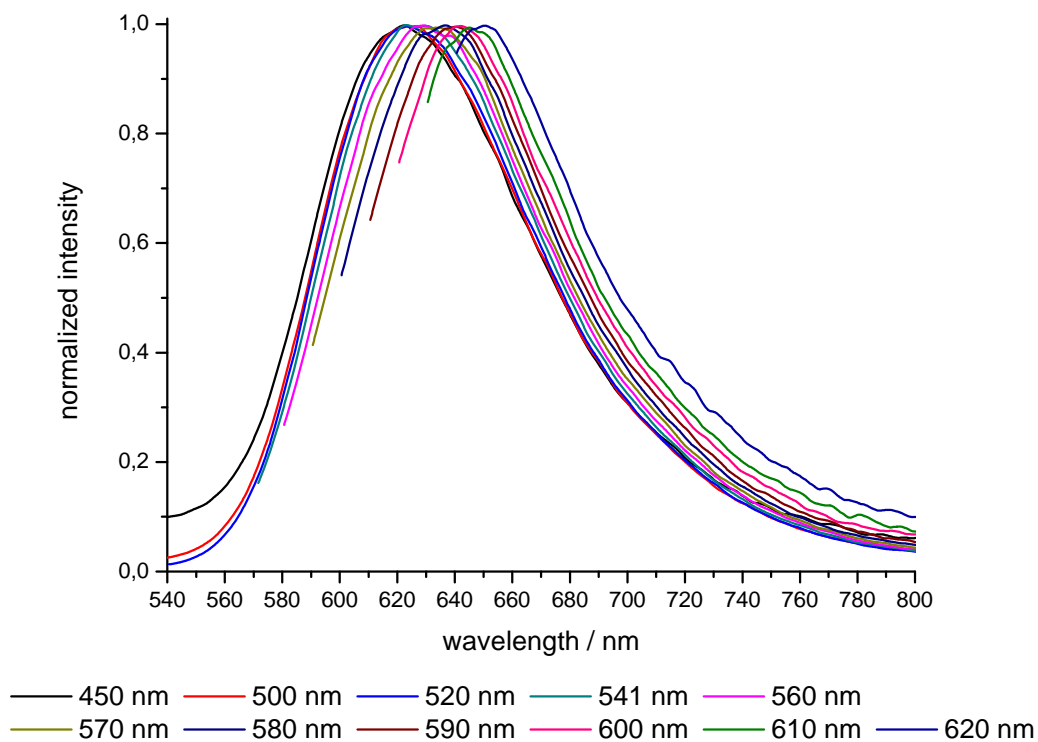


Figure S 41: Fluorescence spectra of **7e** at designated excitation wavelengths showing REES.

## 2.6. Fluorescence quenching of hybrid materials **6b** and **7e**

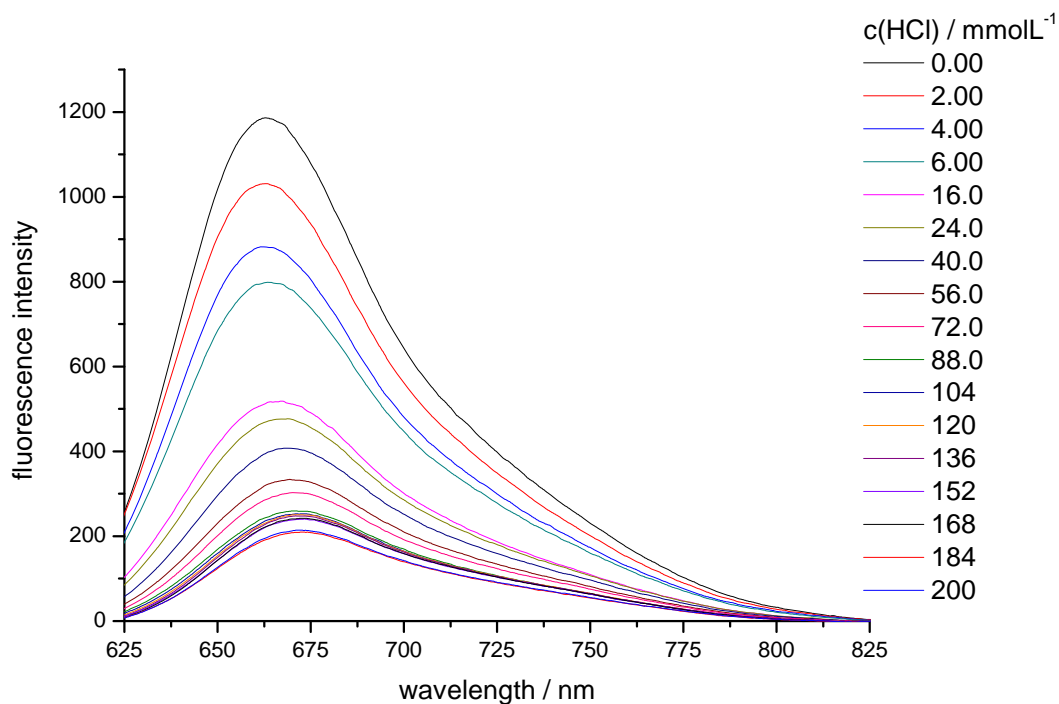


Figure S 42: fluorescence quenching of **6b** in water upon addition of designated amounts of HCl.

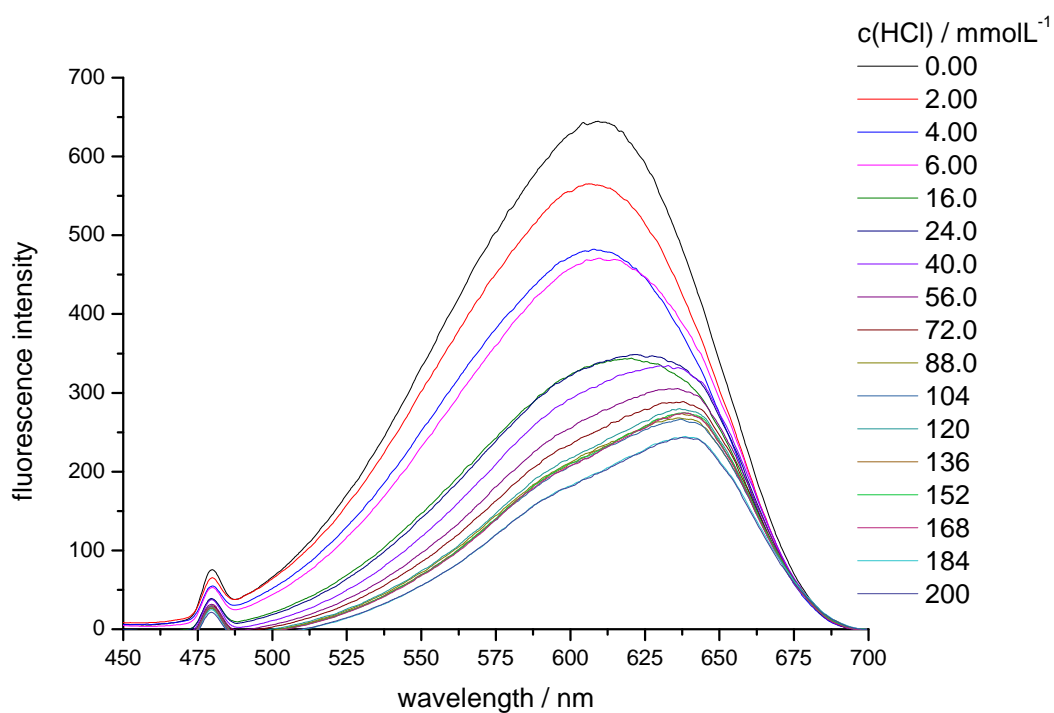


Figure S 43: excitation spectra of fluorescence quenching of **6b** in water upon addition of designated amounts of HCl ( $\lambda_{\text{emission}} = 720 \text{ nm}$ ).



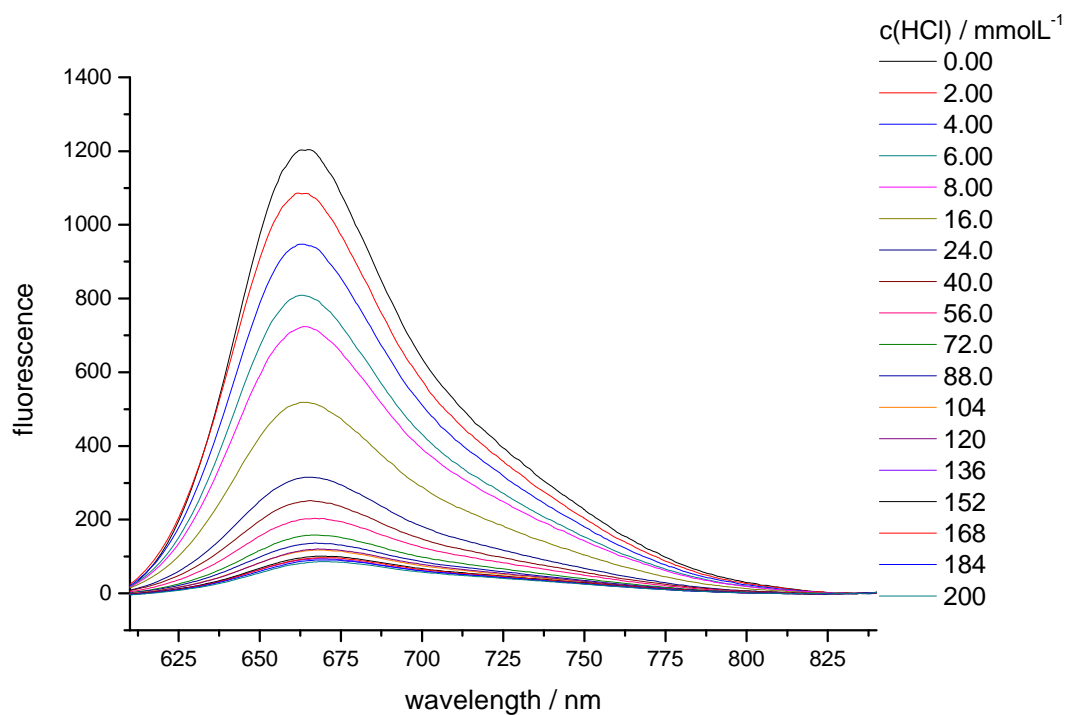


Figure S 44: fluorescence quenching of **7e** in water upon addition of designated amounts of HCl.

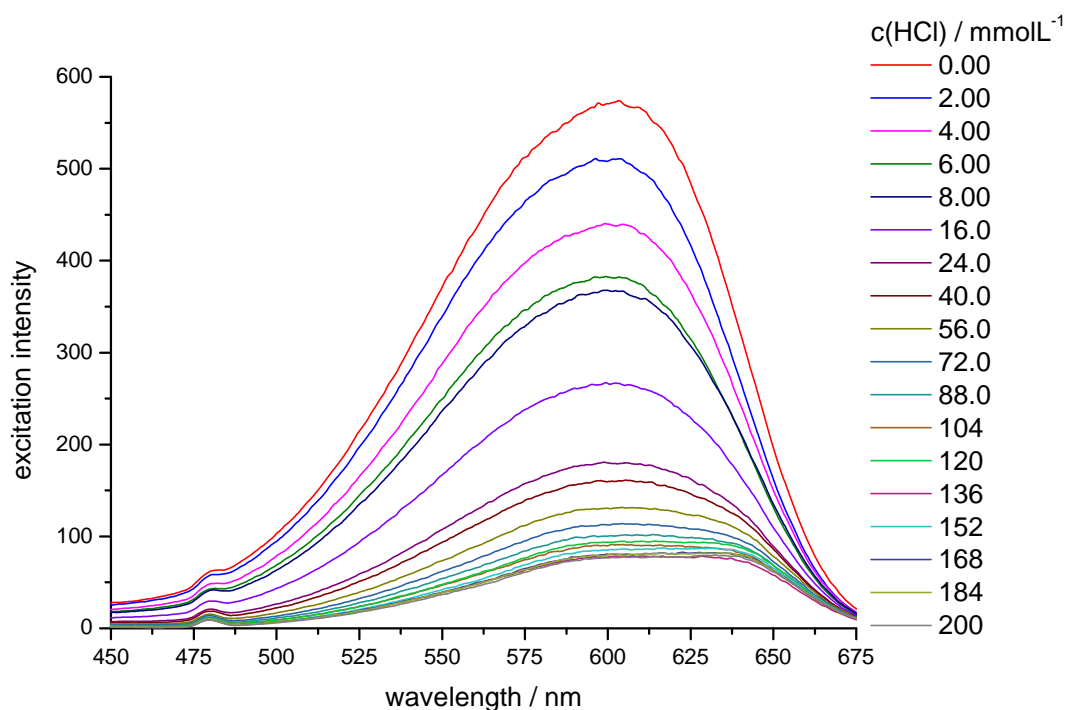


Figure S 45: excitation spectra of fluorescence quenching of **7e** in water upon addition of designated amounts of HCl ( $\lambda_{\text{emission}} = 720 \text{ nm}$ ).