



# Influence of the degree of polymerization and surface curvature on the supramolecular organization of fixated polythiophenes

Jonas Delabie<sup>a</sup>, Julien De Winter<sup>b</sup>, Pascal Gerbaux<sup>b</sup>, Thierry Verbiest<sup>c</sup>, Guy Koeckelberghs<sup>a,\*</sup>

<sup>a</sup> Laboratory for Polymer Synthesis, KU Leuven, Celestijnenlaan 200F, Box 2404, B-3001, Heverlee, Belgium

<sup>b</sup> Organic Synthesis and Mass Spectrometry Laboratory, Research Institute for Materials Science and Engineering, University of Mons-UMONS, 23 Place de Parc, B-7000, Mons, Belgium

<sup>c</sup> Laboratory for Molecular Electronics and Photonics, KU Leuven, Celestijnenlaan 200D, Box 2425, B-3001, Heverlee, Belgium

## ABSTRACT

Hybrid conjugated polymer (CP)/nanoparticle (NP) materials are found to be very promising materials displaying enhanced properties that exceed their individual counterparts. Those promising properties depend a lot on the organization of the CP within the hybrid material. However, not a lot is known about the supramolecular organization of CPs grafted onto NP materials. Previous research by Ceunen et al. has indicated a hampered organization, however, only small molecules grafted onto a single type on NP was studied. Additionally, new insights into the supramolecular organization of conjugated polymers (CPs) by addition of nonsolvent have demonstrated that a key step towards supramolecular organization is the formation of polymer-solvent clusters. This new information could provide a satisfactory explanation for the potentially disrupted supramolecular organization of CPs grafted onto nanoparticle surfaces as fixating the CPs prohibits the formation of these polymer-solvent clusters and thus no supramolecular organizations can be formed. In order to prove this hypothesis, an in-depth investigation concerning the supramolecular organization of grafted CPs is performed this manuscript by changing the size of the CPs and the nature and size (and thus surface curvature) of the NP material. The results indicate a strong inhibition of the supramolecular organization upon fixation of the CP polymer, which is in line with the formulated hypotheses.

## 1. Introduction

Many of the interesting photo-electronic properties of conjugated polymers (CPs) originate from their unique supramolecular and mesoscopic organization behavior [1–8]. Therefore, plenty of research has been dedicated towards this topic and continues to draw attention to this day [9–20]. Throughout the years, however, the use of conjugated polymers has evolved from standalone materials towards more hybrid conjugated materials. Especially the combination between the optoelectronic properties and excellent processability of CP with the unique photonic properties of inorganic nanoparticles (NPs) has found a lot of interest in recent years [21–34]. However, only a few studies have been performed regarding the supramolecular organization of conjugated polymers grafted onto nanoparticle materials. Ceunen et al., has demonstrated that conjugated polymer chains grafted onto magnetite NPs can only interact with each other when grafted onto different nanoparticles, meaning no supramolecular organization is observed between CPs attached on the same NP [35]. However, only low molar mass polythiophenes ( $8.4 \text{ kg mol}^{-1}$ ) grafted onto small magnetite NPs ( $\pm 10 \text{ nm}$ ) were used, lacking an overview of the influence of different NP materials and sizes. Another preliminary study performed by our

group investigated the supramolecular behaviour of chiral polyfluorenes grafted onto NPs of different sizes. Although no chiral response could be obtained for the CPs attached to the NP materials, no solid conclusions could be made as even the “free” polymer by itself displayed only minor amounts of supramolecular organization [36]. Nevertheless, both studies seem to indicate that the formation of supramolecular structures of CPs attached to the same NP is impossible, but an in-depth explanation as for the reason why, could not be given.

Recently, however, new insights into the formation process of supramolecular CP aggregates by addition of a nonsolvent have been obtained. While it was previously generally believed that the supramolecular organization of CPs comprises possible planarization of the backbone, resulting in a stronger conjugation,  $\pi$ - $\pi$  interactions between stacked polymer backbones and possible interactions between side-chains, a study performed by Moris et al. revealed that the formation of supramolecular polymer aggregates is instead induced by the formation of structured polymer-solvent clusters, prior to planarization [37]. In addition, the final symmetry present in the resulting aggregates is already present in these cluster. This implies that the formation of these polymer-solvent clusters is the key to the formation of supramolecular CP aggregates and the final particular supramolecular

\* Corresponding author.

E-mail address: [guy.koeckelberghs@kuleuven.be](mailto:guy.koeckelberghs@kuleuven.be) (G. Koeckelberghs).

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organization. These new insights could provide a possible explanation for the suggested inhibited supramolecular organization of CPs grafted onto NP materials. By fixating the CPs to the NP materials, it can be hypothesized that the CPs are inhibited to pre-organize and form these polymer-solvent clusters. As a consequence, no supramolecular organization, and consequently chiral expression, is observed.

However, while previous results do not deny this hypothesis, it does not prove this because the absence of chiral expression might have other origins as well. First, it is well-known that CPs with higher molar masses are more prone to aggregation. Nevertheless, previous research concerning the supramolecular organization of CPs grafted onto NP materials only used low molar mass CPs (to guarantee end-group fidelity), leaving the possibility that the CPs are simply too short to provide a good organization when attached to the NPs. Second, also the size of the NPs could be a determining factor as it influences the surface curvature, and thus the proximity and intermolecular interactions between the grafted polymer chains. Finally, the molecular structure, including the binding group, must be exactly the same, as previous research has indicated that the end-group has a large influence on the supramolecular organization of conjugated polymers [38].

Therefore, this manuscript aims to investigate these influences by investigating the chiral expression of poly(3-((S)-3,7-dimethyloctyl)thiophene)s, of different degrees of polymerizations (DP = 15, 30, 50 and 70) grafted onto magnetite and silica NPs and a flat glass substrate. The magnetite NP are small ( $16 \pm 3$  nm) and thus have a large surface curvature ( $1.25 \cdot 10^8 \text{ m}^{-1}$ ) compared to the larger silica nanoparticles ( $321 \pm 21$  nm) which have a curvature of  $3.11 \cdot 10^6 \text{ m}^{-1}$  and the glass substrate, which is rather flat (the roughness is 1–2 nm) and has a curvature of  $10^9 \text{ m}^{-1}$ . In order to graft these polymers onto all these different NP materials a universal catechol linker is used, implemented as an end-group onto the polymer chain, which is able to bind to all these materials. Until recently, however, a different end-group was required in order to functionalize all these NP materials, making this study impossible. A recent study by our group, however, proposed catechol as a universal linker molecule which allows for a study of the supramolecular behaviour of grafted CPs on different materials without the influences of the different end-groups [36].

## 2. Results and discussion

### 2.1. Synthesis of polymers

In order to investigate the influence of the DP, a series of poly(3-((S)-3,7-dimethyloctyl)thiophene)s with aimed DP of 15, 30, 50 and 70 is synthesized via a Kumada catalyst transfer condensative polymerization (KCTCP) using a catechol-based external nickel initiator, resulting in polymers **P15**, **P30**, **P50** and **P70** respectively. The controlled nature of the polymerization with an external catechol-based nickel initiator has been established in previous research and allows for easy control over the DP by altering the initial monomer over initiator concentration ratio [35]. Because of the absence of transfer reactions each polymer chain will bear the catechol group at the beginning of the chain, meaning quantitative implementation of the catechol end-group can be obtained. Note that the catechol group is protected with acetyl groups, as the hydroxyl groups are not compatible with the Grignard reagent used in

the KCTCP process.

**Table 1** gives an overview of the molar mass, dispersity and obtained DP after purification via Soxhlet extraction in subsequently methanol and chloroform. The molar mass is measured using GPC and is slightly overestimated due to the rigid nature of polythiophene compared to the used polystyrene standards [39]. The results demonstrate the advantages of the controlled nature of the polymerization as the obtained DP is in close proximity with the initially aimed DP while maintaining an overall low dispersity around 1.1.

Additionally, the presence of the catechol group was confirmed using both  $^1\text{H}$  NMR and MALDI-ToF (See supporting information) in the same way as reported in earlier research [35,36,40]. Although the catechol end-group is successfully and almost quantitatively implemented, partial deprotection of the hydroxyl groups during the polymerization is observed (Fig. 1). A similar observation can be made based on the recorded MALDI mass spectra (Figs. S6–S9). The ratio of deprotected catechol seems to increase for the higher degrees of polymerization, as confirmed by NMR and mass spectroscopy. The cause of the deprotection is two-fold. First, the polymerization is terminated using HCl, causing acidic circumstances which can lead to deprotection of acetyl groups. Because lower initiator concentrations are used for the synthesis of the higher DP polymers, a lower polymer concentration is obtained. However, the same amount of HCl is added to quench each polymerization, which means that the proportion of HCl is much larger for the higher DP polymerizations, leading to increased deprotection. A second reason is a reaction of the acetyl protection groups with the Grignard monomer. Although the acetyl groups are meant to avoid deactivation of the monomers, this side-reaction is still possible. Because the polymers with higher DPs are made using a higher initial monomer over catechol initiator ratio, a larger fraction of the hydroxyl groups will be deprotected. It is important to note that although there is a possible side reaction with the Grignard monomer, this still proceeds much slower than the actual polymerization reaction. As a consequence, it remains possible to very accurately obtain the desired polymers with a low dispersity. Other silane-based protective groups have been considered as well, which do not react with the Grignard monomer. However, these do not significantly reduce the electron donating nature of the hydroxyl groups, making the oxidative insertion into the nickel catalyst impossible.

### 2.2. Synthesis and analysis of the hybrid materials

Next, the synthesized polymers are used to graft onto magnetite and silica NPs via an in-situ deprotection of the hydroxyl groups using ammonia, as described previously [41]. All materials are washed thoroughly with THF to remove any remaining free polymer, after which the hybrid materials are investigated using UV-Vis and fluorescence spectroscopy. The results of the UV-Vis analysis of the hybrid magnetite and silica NPs is represented in Fig. 2. For the hybrid silica NPs there is a clear contribution of the conjugated polymer. This becomes even more apparent when subtracting the spectrum of pure silica NPs from the spectra of the hybrid materials, displaying only the polymer contribution. The obtained spectra closely resemble the spectra of the free polymer, which indicates a successful functionalization. At first sight there does not seem to be a defined polymer peak in the UV-Vis spectra of the hybrid magnetite NPs. However, upon looking at the difference between the pure magnetite NPs and the hybrid magnetite NPs a clear polymer contribution is observed. Note that for both hybrid NPs a blue shift of the polymer peak is observed compared to the free polymer. This can be explained by the inherent Rayleigh scattering of the nanoparticle materials, which is more intense at smaller wavelengths. Additionally, the Rayleigh scattering of the hybrid NPs and the original NPs is different due to the functionalization with the polymer, which can lead to an apparent blue-shift when subtracting the UV-Vis of the original nanoparticles from the hybrid material. In addition to UV-Vis analysis, the fluorescence measurements also confirm the presence of the

**Table 1**

Molar mass ( $M_n$ ), dispersity ( $\mathcal{D}_M$ ) and obtained degree of polymerization for polymers **P15**, **P30**, **P50** and **P70**.  $^\dagger$ determined with GPC towards polystyrene standards.  $^{††}$ Determined with  $^1\text{H}$  NMR.

	$M_n$ (kg.mol $^{-1}$ ) $^\dagger$	$\mathcal{D}_M$	Obtained DP $^{††}$
P15	4.1	1.13	13
P30	8.5	1.08	31
P50	14.1	1.09	53
P70	19.9	1.1	66

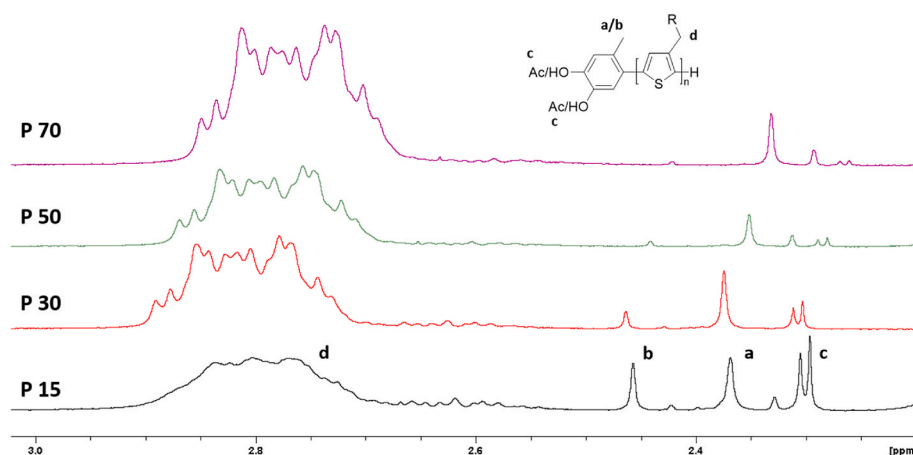


Fig. 1.  $^1\text{H}$  NMR analysis of P15, P30, P50 and P70 between 3 and 2.3 ppm, displaying the deprotection of the hydroxyl groups during the polymerization.

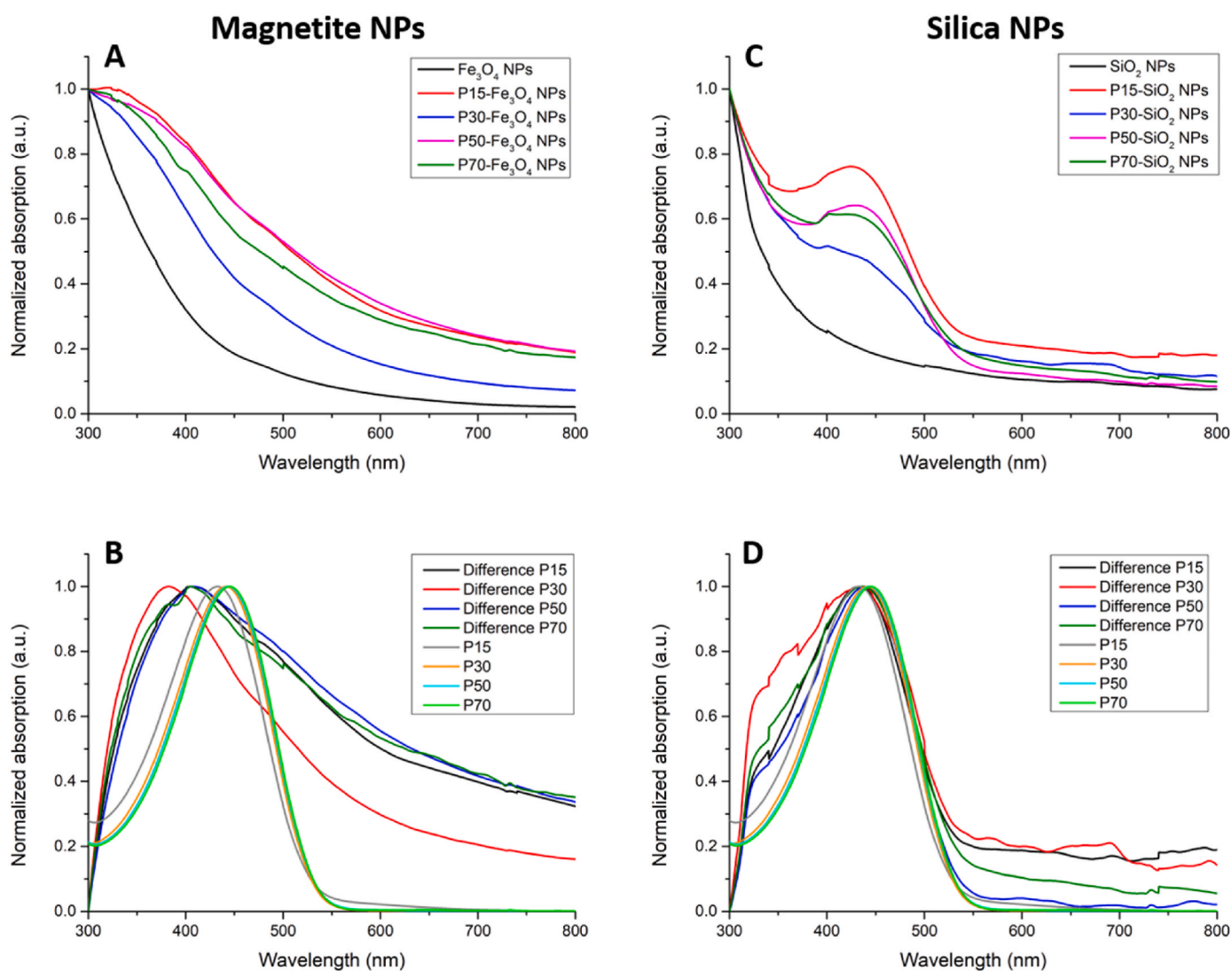


Fig. 2. UV-Vis spectra of LEFT – A) Magnetite NPs before and after functionalization. B) Difference between hybrid magnetite NPs and the non-functionalized magnetite NPs compared to the free polymer. RIGHT – C) Silica NPs before and after functionalization. D) Difference between hybrid silica NPs and the non-functionalized magnetite NPs compared to the free polymer. All UV-Vis spectra are recorded in THF.

conjugated polymer (Fig. S10). A similar shape of the fluorescence band is observed for both the pure polymers and the hybrid materials, indicating a similar conformation of the polymer is adapted for all materials when dissolved or dispersed in THF.

The grafted glass plates are synthesized by submerging the glass plates, cleaned with nochromix and  $\text{H}_2\text{SO}_4$ , into a polymer solution in THF in the presence of ammonia to deprotect any remaining protected hydroxyl groups. The glass plates are subsequently washed with THF and dried under nitrogen flow prior to the UV-Vis analysis (Fig. 3). Once more, a clear contribution of the different polymers is observed on UV-Vis after functionalization. However, the signal is much weaker compared to the nanoparticle materials or other spin-coated materials as the grafting technique only deposits a single monolayer of polymer. Due to the low intensity, some artefacts in the spectrum are observed that can be contributed to the switching between lamps on the spectrophotometer. These artefacts are omitted from the spectrum to better demonstrate the presence of the polymer, however, the original data can be found in the supporting information (Fig. S19).

### 2.3. Study of the supramolecular behavior

In order to better understand the supramolecular behavior of grafted polythiophenes, solvatochromism experiments are performed and compared to the free polymer. This is done by gradually adding MeOH as a non-solvent at a consistent rate of 0.20 ml/min to either the free polymers or the hybrid nanoparticle materials grafted with **P15**, **P30**, **P50** and **P70**. UV-Vis and circular dichroism (CD) measurements are subsequently recorded at 0, 10, 20, 30, 40, 50, and 60% MeOH concentrations. The results for **P15**, **P30**, **P50** and **P70** and their corresponding hybrid magnetite and silica NPs are displayed in Figs. 4–7. As expected a clear red-shift and chiral expression is observed at higher MeOH concentrations for all the free polymers, indicating the formation of chiral supramolecular structures. Additionally, the increased vibrational fine structure for the high molar mass polymers indicates a larger fraction of crystalline, and thus organized supramolecular structures, which is in line with previously reported studies. The relative intensity of the band near  $\sim 625$  nm is a good (qualitative) measure for the trend in fraction of crystallized polymer as only crystallized poly(3-alkylthiophene)s absorb at that region. Note that the absence of the isosbestic point can be explained by precipitation of the polymers at higher MeOH concentrations, which is especially the case for **P50** and **P70**. Very interestingly, while these UV-vis spectra reveal a (known) trend of increasing degree of crystallinity upon increasing the degree of

polymerization, the CD spectra provide valuable information on the chiral organization within the aggregates. Briefly stated, the intensity of  $\Delta\epsilon$  depends on the amount of chirally organized material and on the way these polymer organizes. Since both  $\epsilon$  and  $\Delta\epsilon$  scale linearly with the amount of crystalline material,  $g_{\text{abs}}$  ( $g_{\text{abs}} = \Delta\epsilon/\epsilon$ ), measured in a region where only crystallized polymer absorbs (e.g.  $\sim 625$  nm), is a direct, qualitative measure of how the polymer chains are chirality organized.  $g_{\text{abs}}$ , measured at 625 nm, equals  $5 \cdot 10^{-3}$ ,  $6 \cdot 10^{-3}$ ,  $3 \cdot 10^{-3}$  and  $2 \cdot 10^{-3}$  for **P15**, **P30**, **P50** and **P70**, respectively. This immediately shows that the degree of polymerization not only affects the amount of supramolecularly polymer, but also the organizational architecture itself.

Upon fixating the CPs onto the NPs, no chiral expression and red-shift, and thus no organized supramolecular organization is observed, even for the high molar mass polymers. Note that for the hybrid  $\text{SiO}_2$  NPs high extinction coefficients are observed at higher MeOH concentrations. This can be attributed to Mie-scattering which coincides with appearance of a milk-white opaque dispersion of the  $\text{SiO}_2$  NPs upon addition of MeOH.

Finally, to analyze the influence of the curvature, the supramolecular organization of **P15**, **P30**, **P50** and **P70** grafted onto glass plates is investigated by submerging the samples in subsequently THF, 50% THF/MeOH and pure MeOH, each time measuring UV-Vis and CD spectroscopy and compared with the results of the hybrid magnetite and silica NPs. The results are displayed in Fig. 8 and clearly demonstrate that even for a flat surface no chiral response is obtained. Nevertheless, looking at the UV-Vis spectra a red-shift can be observed, indicating a change in conformation of the polymer chains. However, the absence of vibrational fine structures in the spectra indicates the absence of supramolecular organization and thus the red-shift originates purely from planarization of the individual polymer chains.

Because neither the DP of the polymer, which affects both the fraction of aggregated polymer and their organization, nor the nature and the curvature of the surface, results in a chiral expression – although the molecular structure, including anchoring group, remains untouched – it can be concluded that fixating the conjugated polymer onto a surface prevents it from forming organized supramolecular structures. Furthermore, the UV-Vis analysis of the polymers grafted onto the glass substrate clearly demonstrates (some) planarization of the individual polymer chains. While this is usually immediately followed by the formation of supramolecular aggregates, this is not observed upon fixating the polymer chains. This means that a unique system is obtained in which planarization of the individual polymer chains can be achieved without the formation of supramolecular organization. It also confirms our hypothesis that due to the fixation, the polymers are unable to form the crucial polymer-solvent clusters required to obtain supramolecular stacking of the polymer chains. This implies that no matter on which surface the CPs are grafted, it will be impossible to obtain chiral expression of aggregates obtained by addition of a nonsolvent. This contrast with spin coated or drop casted CPs as they are not directly fixated to the surface and thus retain the freedom to form the favorable polymer-solvent clusters before evaporation of the solvent.

### 3. Conclusion

To summarize the results, it can be concluded that chiral supramolecular organization of polymer chains fixated onto the same surface is impossible. Even for larger polymer chains, no chiral expression is observed for the hybrid materials and changing curvature of the surface does not seem to improve the results either. An explanation is found in the fact the fixation of the polymer chains impedes the formation of polymer-solvent clusters that precede the formation of supramolecular aggregates as demonstrated in earlier research. These results imply that, no matter the surface or length of the polymer chain, supramolecular organization of fixated conjugated polymers is impossible. Nevertheless, because planarization is still possible for individual polymer chains fixated onto a flat surface, a unique system is achieved in which

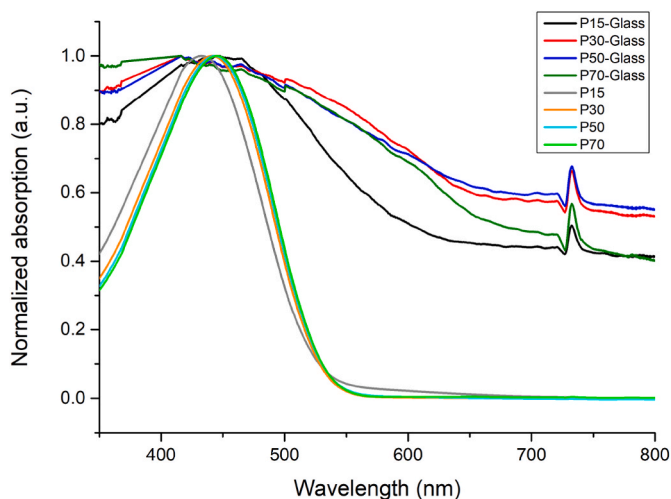
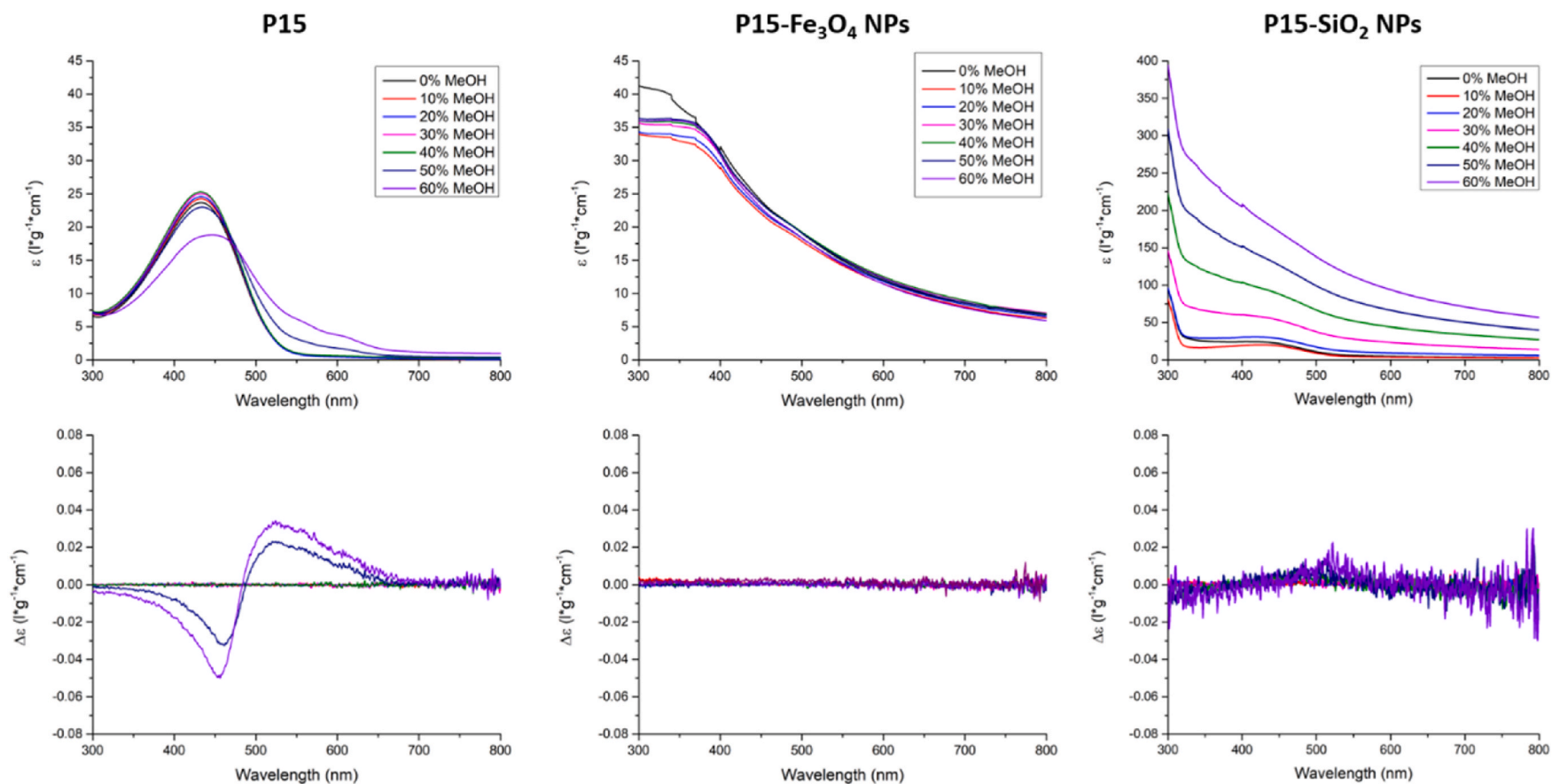
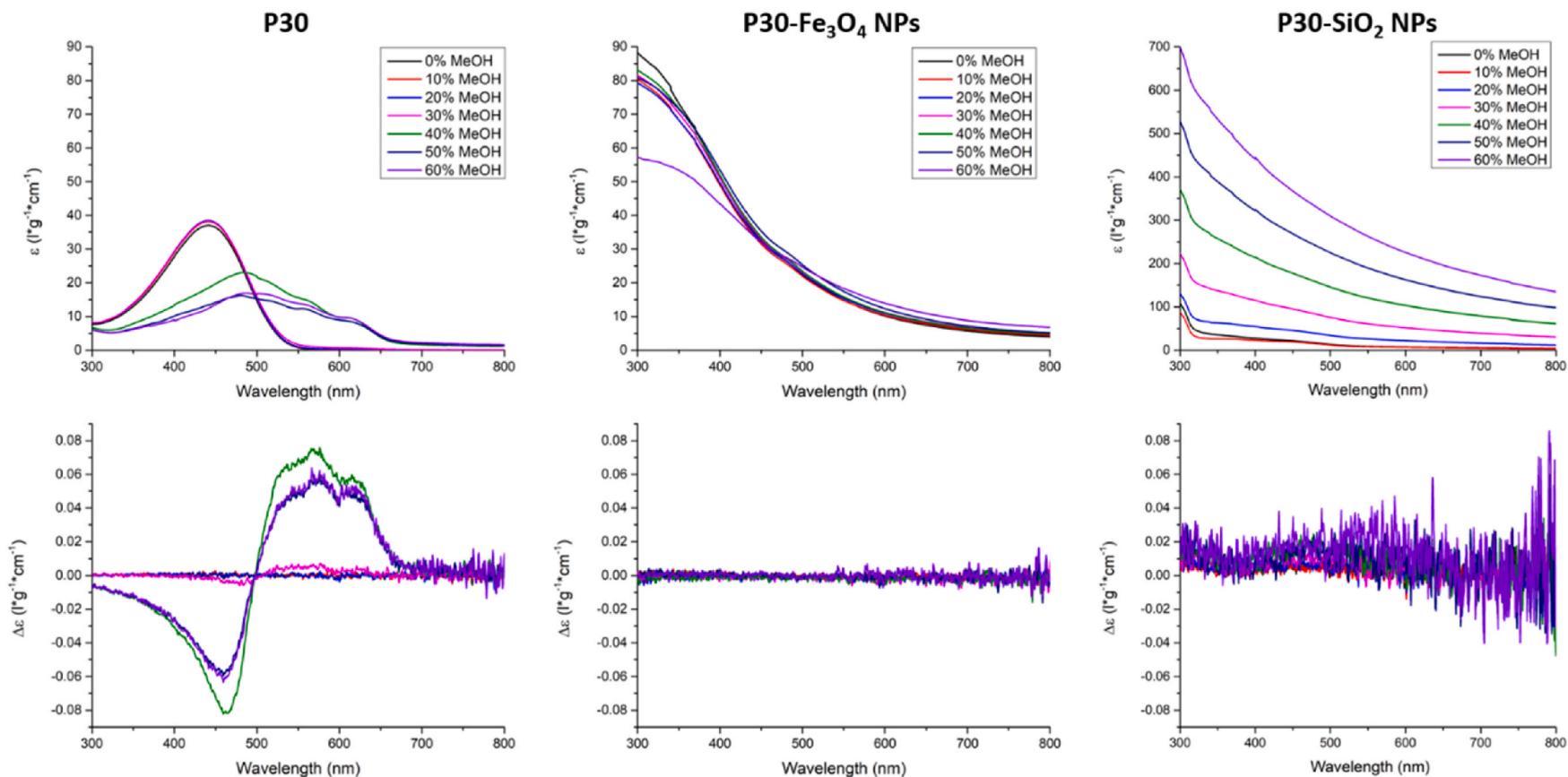


Fig. 3. Normalized UV-Vis spectra of glass plates functionalized with **P15**, **P30**, **P50** and **P70**, measured under normal atmosphere and compared with the pure polymers dissolved in THF.

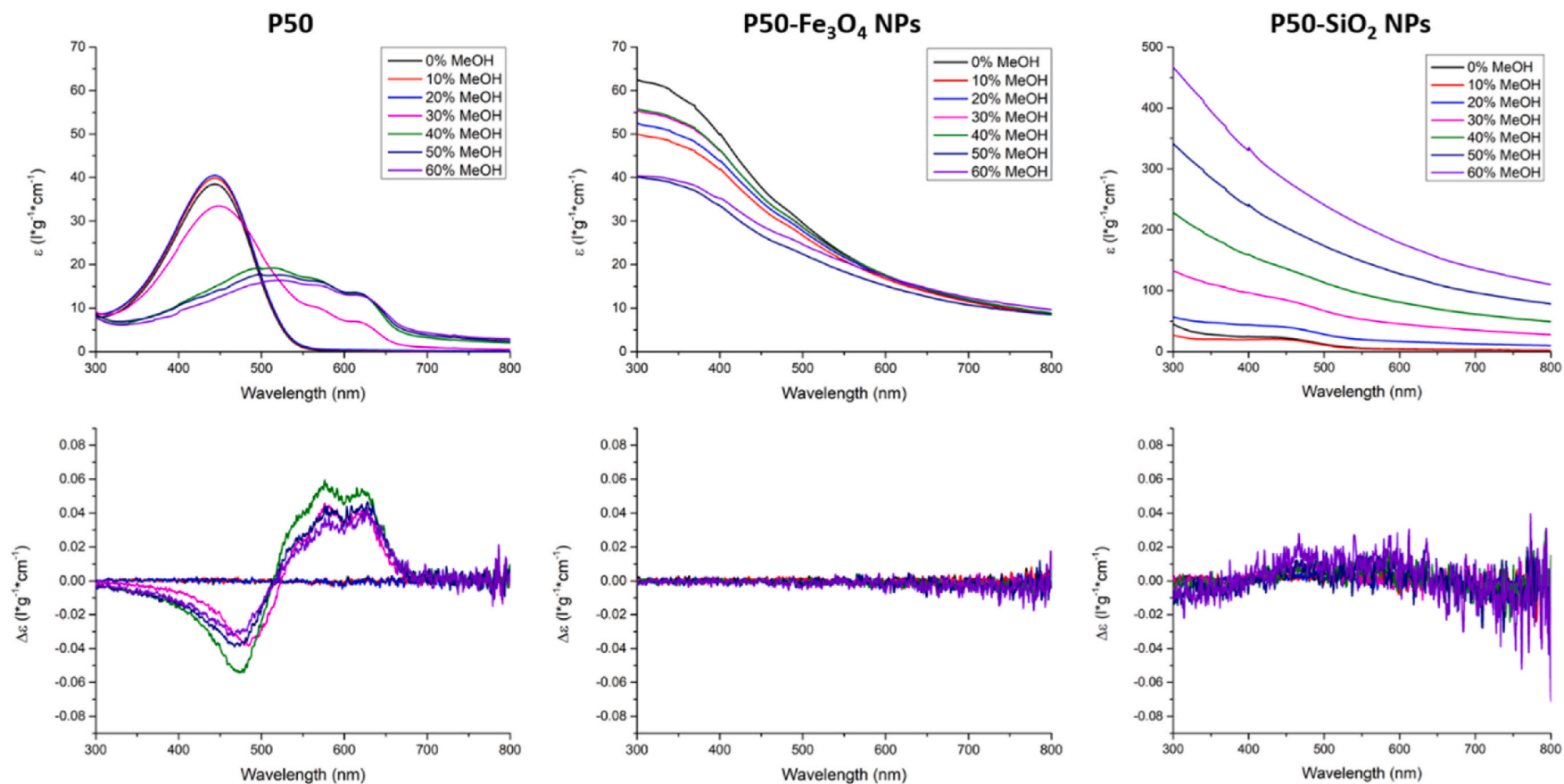




**Fig. 4.** Overview of the UV-Vis (TOP) and CD (BOTTOM) analysis of the solvatochromism experiments of P15, P15-Fe<sub>3</sub>O<sub>4</sub> NPs and P15-SiO<sub>2</sub> NPs dissolved or dispersed in THF with MeOH as a non-solvent.



**Fig. 5.** Overview of the UV-Vis (TOP) and CD (BOTTOM) analysis of the solvatochromism experiments of P30, P30-Fe<sub>3</sub>O<sub>4</sub> NPs and P30-SiO<sub>2</sub> NPs dissolved or dispersed in THF with MeOH as a non-solvent.



**Fig. 6.** Overview of the UV-Vis (TOP) and CD (BOTTOM) analysis of the solvatochromism experiments of P50, P50-Fe<sub>3</sub>O<sub>4</sub> NPs and P50-SiO<sub>2</sub> NPs dissolved or dispersed in THF with MeOH as a non-solvent.

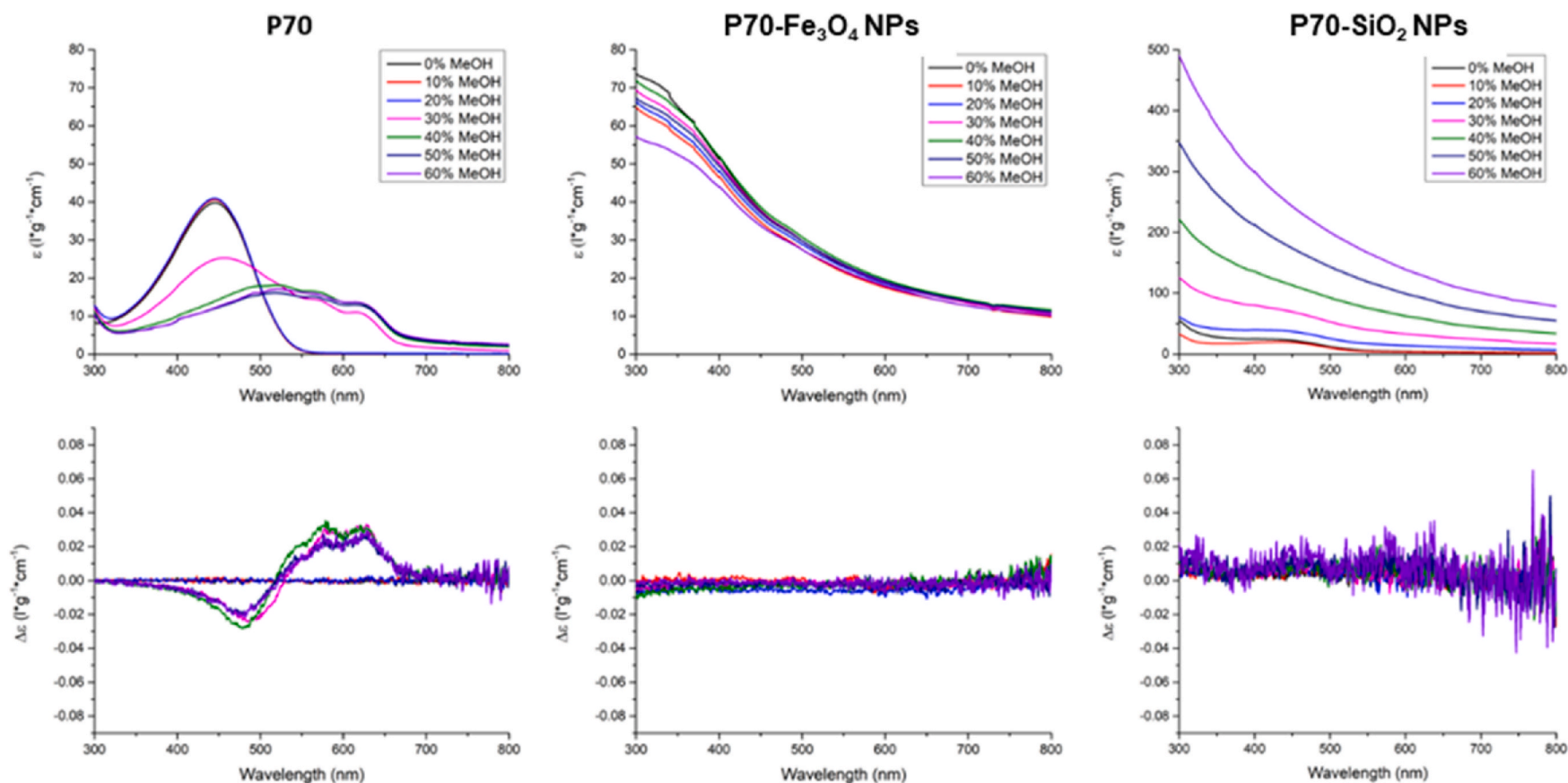
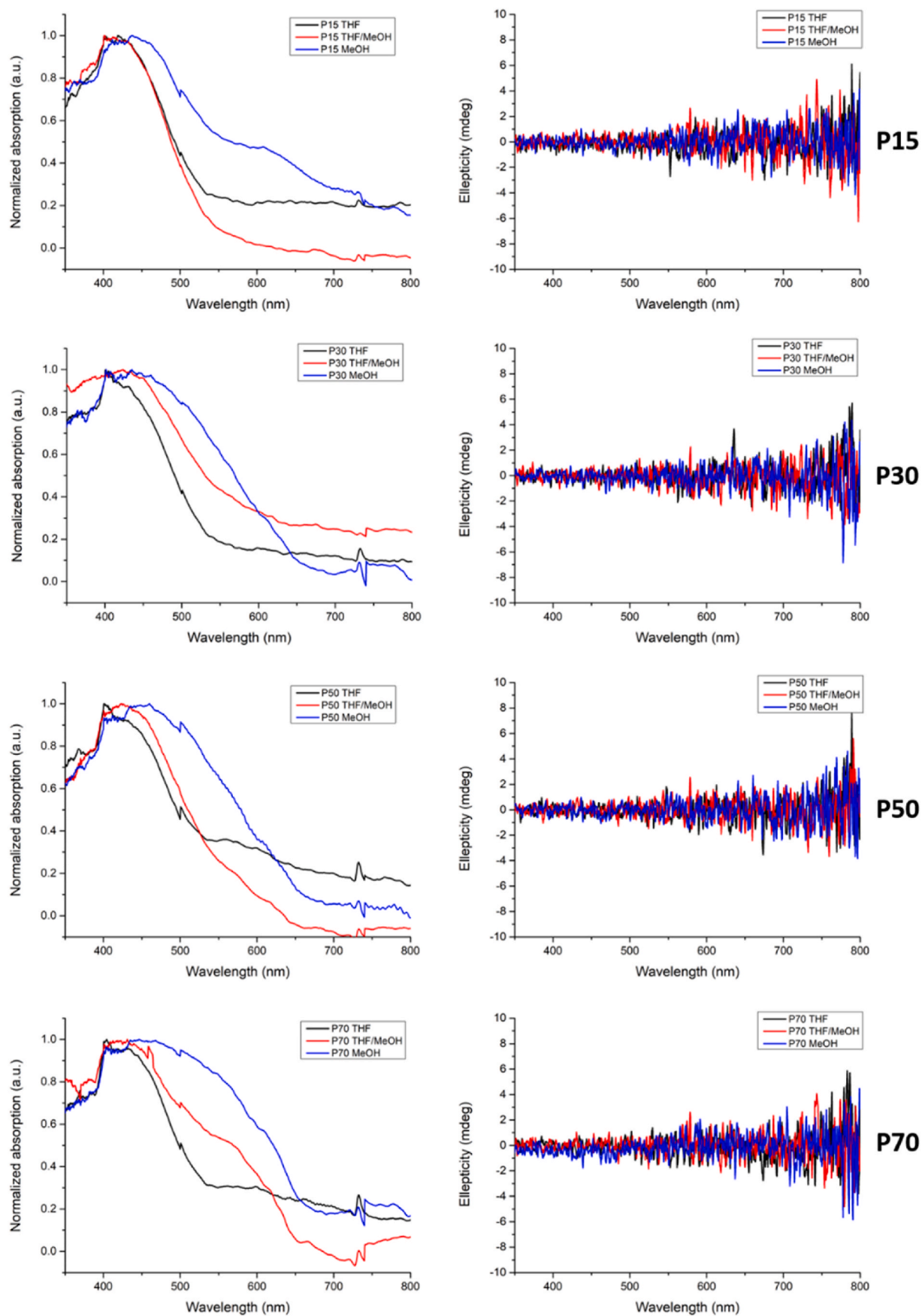


Fig. 7. Overview of the UV-Vis (TOP) and CD (BOTTOM) analysis of the solvatochromism experiments of P70, P70-Fe<sub>3</sub>O<sub>4</sub> NPs and P70-SiO<sub>2</sub> NPs dissolved or dispersed in THF with MeOH as a non-solvent.





**Fig. 8.** UV-Vis (LEFT) and CD (RIGHT) spectra of **P15**, **P30**, **P50** and **P70** grafted onto flat glass substrates submerged into subsequently THF, 50% THF/MeOH and MeOH.

planarized conjugated polymer chains do not form supramolecular aggregates. This is a unique effect that is impossible to achieve in solution and could potentially allow the study of the properties of single conjugated polymer chains.

### CRediT authorship contribution statement

**Jonas Delabie:** conducting the synthesis and most experiments, writing the manuscript. **Julien De Winter:** MALDI-ToF measurements and interpretation, correcting the manuscript. **Pascal Gerbaux:** MALDI-ToF measurements and interpretation, correcting the manuscript. **Thierry Verbiest:** Supervision, of the nanoparticle synthesis and characterization, correcting the manuscript. **Guy Koeckelberghs:** global supervision, Supervision, of synthesis and most experiments, correcting the manuscript.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

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## References

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- ## CRediT authorship contribution statement
- Jonas Delabie:** conducting the synthesis and most experiments, writing the manuscript. **Julien De Winter:** MALDI-ToF measurements and interpretation, correcting the manuscript. **Pascal Gerbaux:** MALDI-ToF measurements and interpretation, correcting the manuscript. **Thierry Verbiest:** Supervision, of the nanoparticle synthesis and characterization, correcting the manuscript. **Guy Koeckelberghs:** global supervision, Supervision, of synthesis and most experiments, correcting the manuscript.
- ## Declaration of competing interest
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- ## Appendix A. Supplementary data
- Supplementary data to this article can be found online at <https://doi.org/10.1016/j.polymer.2022.124846>.
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