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Chiral Poly(4-ethynylbenzoyl-L-valine)-Induced Helical Self-Assembly of Alkynylplatinum(II) Terpyridyl Complexes with Tunable Electronic Absorption, Emission, and Circular Dichroism Changes

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Abstract: A chiral amino acid-containing polyacetylene, poly(4-ethynylbenzoyl-L-valine), was found to induce the aggregation and self-assembly of square-planar alkynylplatinum(II) terpyridyl complexes by electrostatic binding of the positively charged metal complexes to the anionic sites of the polyacetylene, as revealed by the appearance of new UV/Vis absorption and emission bands upon mixing under basic conditions. The induced complex self-assembly was found to be influenced by the polyacetylene and/or base concentration, and the effect of pH on the reversibility of the aggregate/monomer interconversion was also studied. The conformational changes of the polyacetylene were probed by circular dichroism (CD) spectroscopy, in which the chirality signal of the corresponding chain helicity in the presence of the base was enhanced and stabilized upon addition of the platinum(II) complexes. The induced complex aggregation was dependent on the structural properties of the polyacetylene, while the chirality of the polyacetylene was strongly influenced by the introduction of the complex.

Keywords: noncovalent interactions · platinum · polyacetylene ligands · self-assembly · UV/Vis spectroscopy

Introduction

Square-planar d^8 metal complexes have long been known to show a strong tendency in arranging themselves into highly ordered extended linear chain or oligomeric structures in the solid state. Their colors and the corresponding photophysical properties are highly dependent on the extent of the metal–metal and the ligand π–π stacking interactions.[1–14] A particularly interesting class of platinum(II) complexes, which adopts square-planar geometry, has been extensively studied owing to the intriguing spectroscopic and luminescence properties of the monomeric and self-associated states.[5–24]

In the last few decades, luminescent platinum(II) polypyridyl complexes have shed light on the importance of d^8–d^8 metal–metal interactions in governing their spectroscopic behaviors in the solid state.[10–14] Our previous systematic studies on alkynylplatinum(II) terpyridyl complexes have demonstrated the rich solid-state polymorphism as well as interesting solution-state self-assembly properties of this class of compounds, in which induced-aggregation has been shown to be tuned under various conditions, such as solvent composition,[13] counter-anions,[14] and temperature.[25] Recent work also demonstrated the possibility of utilizing synthetic polyelectrolytes or multiple negatively charged biopolymers such as single-stranded nucleic acids and poly(amino acids) in inducing the aggregation of the complexes.[26–28] Remarkable color changes and emission enhancement were observed due to such polyanion-induced self-assembly via metal–metal and π–π stacking interactions in solution.

On the other hand, in the course of our research to synthesize and study helical macromolecules,[29–33] we attached pendants of L-valine, an amino acid commonly found in pro-

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tein, to the skeleton of poly(phenylacetylene) to give amphiphilic polymers, which fold helically and self-assemble into biomimetic morphologies through hydrogen bonding interaction and hybridization of the synthetic conjugated polymers.[34–36] The chain helicity varies with solvent, pH, and temperature, as revealed in the circular dichroism (CD) studies.[37,38]

In the present study, we describe the use of this chiral polyacetylene, poly(4-ethynylbenzoyl-L-valine), that is capable of forming intrastrand and interstrand hydrogen bonds within and between the polymer chains to assume a helical conformation, as a template to induce the self-assembly of the platinum(II) complexes. Three alkynylplatinum(II) complexes, [Pt(tpy)(C≡C−C≡CCH$_2$OH)]OTf (**1**), [Pt(tpy)(C≡C−C≡CH)]OTf (**2**), and [Pt(*t*Bu$_3$tpy)(C≡C−C≡CH)]OTf (**3**) (Scheme 1; tpy = 2,2′:6′,2″-terpyridine; OTf = trifluoromethanesulfonate; *t*Bu$_3$tpy = 4,4′,4″-tri-*tert*-butyl-2,2′:6′,2″-terpyridine), were tested in this investigation. The interaction of the metal complexes with the amino acid-containing polyacetylene was also explored by using UV/Vis absorption, emission, and circular dichroism spectroscopy.

Experimental Section

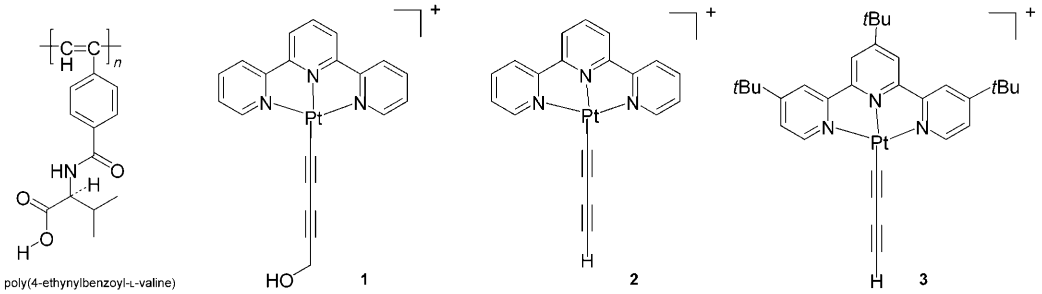
Synthesis: Poly(4-ethynylbenzoyl-L-valine),[34] [Pt(tpy)(C≡C−C≡CCH$_2$OH)]OTf (**1**),[27,28] [Pt(tpy)(C≡C−C≡CH)]OTf (**2**),[13,14] and [Pt(*t*Bu$_3$tpy)(C≡C−C≡CH)]OTf (**3**)[26] were synthesized according to the methods previously described by us.

Instrumentation and physical measurements: UV/Vis absorption spectra were recorded on a Cary 50 (Varian) spectrophotometer equipped with a Xenon flash lamp. Steady-state emission spectra were recorded by using a Spex Fluorolog-3 Model FL3-211 fluorescence spectrofluorometer equipped with a R2658P PMT detector. Unless specified otherwise, the emission spectra were obtained with an excitation wavelength of $\lambda_{ex} > 400$ nm and were corrected for PMT response. Quartz micro-cuvettes with a 10 mm path length and a 2 mm window width were used for UV/Vis and emission measurements. CD measurements were performed on a Jasco 720 CD spectropolarimeter using a cylindrical quartz CD cell with 1 mm path length.

Results and Discussion

Electronic absorption properties: The chemical structures of poly(4-ethynylbenzoyl-L-valine)[34–36] and complexes **1**–**3**[13,14,26,27] used in the present investigation are depicted in Scheme 1. Dissolution of complexes **1**–**3** in an acetonitrile–methanol (1:2, v/v) mixture gave yellow solutions with an intense UV/Vis absorption band at about 285–350 nm and a low-energy absorption band at about 400–414 nm at 298 K. With reference to previous spectroscopic work on platinum(II) terpyridyl alkynyl systems,[13–26] the higher energy absorption band is assigned as π→π* intraligand (IL) transitions of the terpyridine and alkynyl ligands, while the lower energy absorption band is assigned as a dπ(Pt)→π*(tpy) metal-to-ligand charge transfer (MLCT) transition, with mixing of an alkynyl-to-terpyridine ligand-to-ligand charge transfer (LLCT) transition. The observed shift of the energy of the MLCT/LLCT absorption bands in the order of **3** (400 nm) > **2** (406 nm) > **1** (414 nm) is in line with the degree of electron-richness of the substituent on the terpyridine and alkynyl ligands. The highest MLCT/LLCT energy observed for complex **3**, which contains electron-donating *tert*-butyl moieties on the terpyridine ligand, is consistent with the higher-lying π*(*t*Bu$_3$tpy) orbital energy of the *t*Bu$_3$tpy than the terpyridyl ligand in complexes **1** and **2**, while the lower MLCT/LLCT transition energy of **1** than **2** is also consistent with the presence of a more electron-rich hydroxymethylbutadiynyl ligand in complex **1** that raises the dπ(Pt) orbital energy and gives rise to a lower MLCT/LLCT absorption energy. In the solution mixture, complexes **1**–**3** were found to emit at 575, 670, and 665 nm, respectively, upon excitation at $\lambda_{ex} > 400$ nm, which are assigned to originate from an excited state of predominantly ^{3}MLCT character with some mixing of ^{3}LLCT character.

The presence of a solubilizing hydroxymethyl group on the butadiynyl ligand in complex **1** and *tert*-butyl moieties on the terpyridyl ligand in complex **3** was found to improve the solubility of the complexes in methanol, leading to the absence of spectral changes relative to that in the acetonitrile–methanol mixture. On the contrary, as the percentage of acetonitrile in the acetonitrile–methanol mixture was reduced, complex **2** (0.15 mM) showed a decrease in the intensity of the MLCT/LLCT band in the UV/Vis spectra and the emergence of a new lower-energy absorption shoulder in the region of about 480–550 nm. With reference to our previous studies,[13,14,25–28] the emergence of the low-energy absorption shoulder or tail is believed to originate from a metal-metal-to-ligand charge transfer (MMLCT) transition



Scheme 1.

as a result of self-aggregation that gives rise to close Pt···Pt contacts and π···π interactions. The prominent UV/Vis absorption shoulder of complex **2** in methanol at about 0.15 mM is a strong indication of background aggregation. Thus, an acetonitrile–methanol mixture with a 1:2 volume ratio was used in the polyelectrolyte-induced aggregation studies of complex **2**, while complexes **1** and **3** do not encounter any solvent limitation in the present study.

Polyelectrolyte-induced self-assembly studies: Addition of complex **1** or **2** to an equimolar solution of poly(4-ethynylbenzoyl-L-valine) in methanol or acetonitrile–methanol mixture (1:2, v/v) gave rise to a UV/Vis spectrum with absorption bands typical of the complex and the polymer plus a new absorption tail at 500–600 nm. This new absorption tail disappeared when a small amount of acid was added to the corresponding solution mixture. On the other hand, a more intense absorption shoulder appeared in the same region upon addition of a base (Figure 1). Concomitant with the remarkable UV/Vis absorption changes at different pH, new emission bands at about 800 nm in the near-infrared (NIR) region emerged upon mixing the platinum(II) complexes and the polymer, and consistent with the UV/Vis studies, the intensity of these low-energy NIR emission bands was found to be enhanced in the presence of a base but faded away with acid. Figure 2 shows the emission spectra of complex **1** mixed with the polymer under different conditions. When mixed with the polymer only, the mixture of complex **1** showed a weak emission band at about 770 nm, whereas significant emission enhancement with a slight red shift to about 790 nm was observed upon addition of a base. The emission band also diminished when acid was added into the complex mixture. On the basis of our previous work and other related studies,[10–14,25–28] the newly formed UV/Vis shoulders of complexes **1** and **2** at longer wavelengths are assigned as MMLCT transitions, as a result of the aggregation of the complexes induced by the polyelectrolyte through metal···metal and π···π interactions. Consequently, the NIR emission bands are attributed to triplet MMLCT phosphorescence.

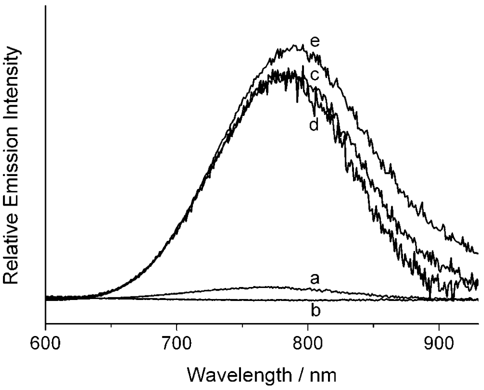


Figure 2. Emission changes of complex **1** (concentration = 0.15 mM) in methanol upon addition of equimolar concentrations of: a) polyacetylene (line a); b) polyacetylene + HCl (line b); c) polyacetylene + KOH (line c); d) polyacetylene + TBAH (line d); e) polyacetylene + NEt_3 (line e).

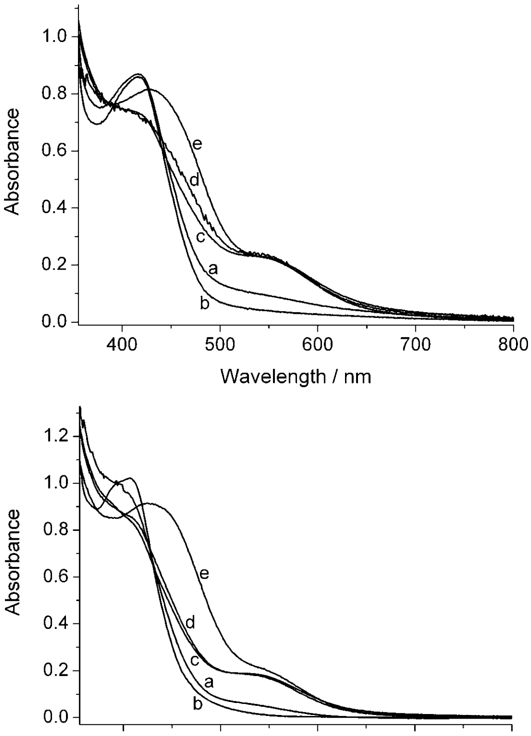


Figure 1. Top: UV/Vis absorption changes of complex **1** (concentration = 0.15 mM) in methanol upon addition of equimolar concentrations of: a) polyacetylene (line a); b) polyacetylene + HCl (line b); c) polyacetylene + KOH (line c); d) polyacetylene + TBAH (line d); e) polyacetylene + NEt_3 (line e). Bottom: UV/Vis absorption changes of complex **2** (concentration = 0.15 mM) in acetonitrile–methanol (1:2, v/v) mixture upon addition of equimolar concentrations of: a) polyacetylene (line a); b) polyacetylene + HCl (line b); c) polyacetylene + KOH (line c); d) polyacetylene + TBAH (line d); e) polyacetylene + NEt_3 (line e).

The amino acid moiety of poly(4-ethynylbenzoyl-L-valine) would exist as the anionic form under conditions that are more basic than its isoelectric point, which in turn, would lead to the disruption of the hydrogen bonds brought about by the electrostatic repulsion between the negative charges, giving rise to random polymer chains. Upon addition of the cationic platinum(II) complexes, charge neutralization would occur as the cationic platinum(II) complexes are electrostatically attracted to the anionic sites of the polyacetylene, inducing self-assembly of the complexes (Figure 3). Addition of HCl converts the amino acid to its cationic form, causing the reversible color and spectral changes as a result of deaggregation. Several bases, namely tetrabutylammonium hydroxide (TBAH), potassium hydroxide, and triethylamine were investigated in this study, and it was found that these bases gave similar to identical spectral changes (Figure 1).

The aggregation process was reversible as confirmed by the on/off switching of the MMLCT band in the UV/Vis ab-

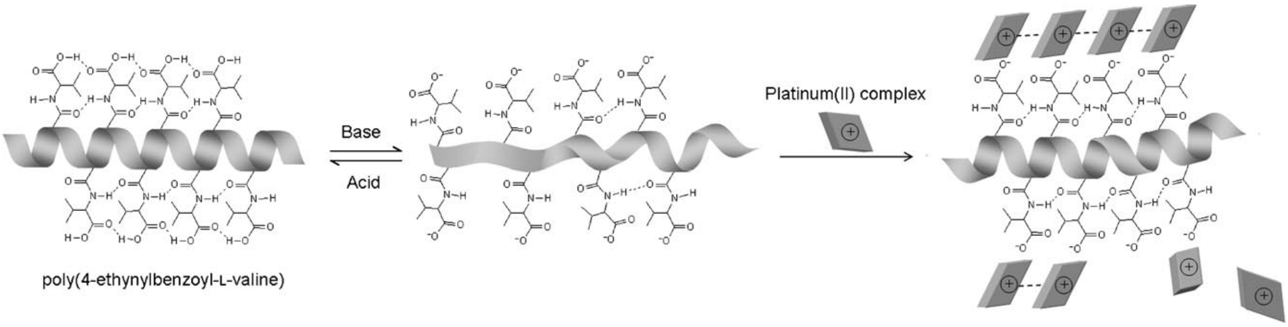


Figure 3. Proposed polyacetylene chain helicity modulation and aggregation of cationic platinum(II) complex ions upon pH adjustment and metal complex addition.

sorption studies upon alternate addition of acids and bases with at least eight repeating cycles under constant ionic strength (Figure 4). Reversible interconversions between the yellowish orange aggregative state and pale yellow monomeric state that could be completed within seconds were observed. The effect of ionic strength on the polyelectrolyte-induced complex self-assembly was also studied. For a mixture of 0.15 mM of complex **1** and polyacetylene with KOH, the MMLCT band in the UV/Vis absorption spectra showed a slight drop in intensity with an isosbestic point at 455 nm with increasing concentrations of KCl in the solution mixture. More significant spectral changes were observed in the emission spectra (Figure 5), which showed a large diminishment of the ^{3}MMLCT emission at high KCl content, indicating that the bound complex molecules were gradually displaced by potassium ions under conditions of high KCl concentration.

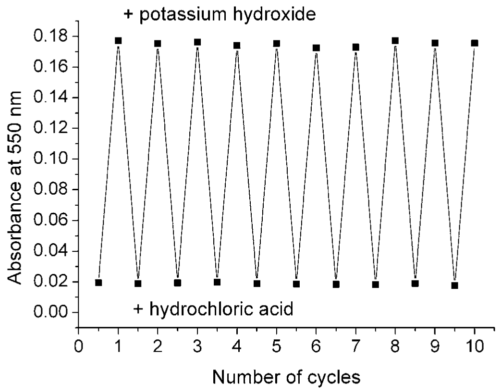


Figure 4. UV/Vis absorption changes of complex **1** and polyacetylene in methanol with alternate addition of hydrochloric acid and potassium hydroxide for eight repeating cycles.

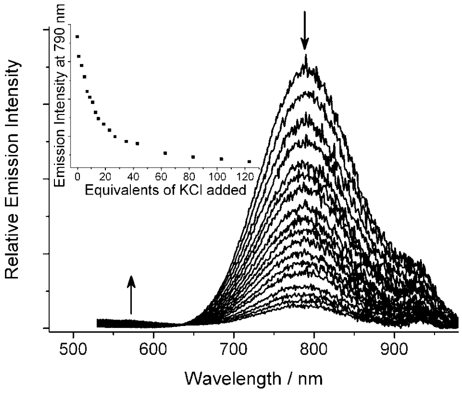


Figure 5. Emission changes of the mixture of complex **1** and polyacetylene in methanol with KOH with increasing KCl concentration (concentration of complex **1**, polyacetylene and KOH concentration: 0.15 mM). Inset: Plot of corrected emission intensity at 790 nm as a function of potassium chloride concentration.

Addition of acid or base into a mixture of complex **3** and poly(4-ethynylbenzoyl-L-valine) did not yield any observable color and spectroscopic changes, confirming that the changes observed in **1** and **2** were a result of aggregate formation as it is well known that the bulky *tert*-butyl moieties on the terpyridine ligand in complex **3** would hinder aggregate formation.

Effect of polymer/complex ratio: The optimization of the ratio between the platinum(II) complexes and the polyacetylene for the aggregation process was performed by monitoring the changes in the UV/Vis absorption spectra. Figure 6 depicts a gradual increase of the MMLCT band intensity when 0 to 3 molar equivalents of polymer (based on valine units) and base were added to complex **1** at 0.15 mM. It was noticed that a clean isosbestic point at about 446 nm could be obtained by adding less than one equivalent of polymer (based on valine units), while deviation occurred with further addition. In this range of molar ratio studied, the increase of polymer units would result in a higher degree of ordering of the complex and a well-defined spectrum of the solution aggregates could be obtained at a 1:1 complex/amino acid unit molar ratio. Owing to the absorption of the polyacetylene backbone, further increase of poly(4-ethynylbenzoyl-L-valine) would cause a large absorbance increase in the ultraviolet and blue region, which in fact would undesirably mask the absorption bands attributed to the platinum(II) complexes.

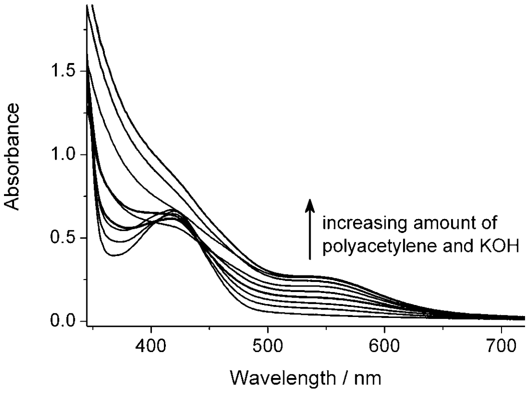


Figure 6. UV/Vis absorption changes of complex **1** (concentration = 0.15 mM) in methanol upon addition of various amounts of polyacetylene and KOH (0, 0.1, 0.2, 0.5, 0.8, 1, 2 and 4 equivalents, respectively).

Effect of KOH concentration: The influence of the base concentration on the self-assembly properties of the platinum(II) complexes was also investigated. By maintaining a constant equimolar concentration of complex **1** and polyacetylene (base on valine units), UV/Vis spectral studies showed a growing MMLCT band with a concomitant decrease in the MLCT/LLCT transition (or "monomeric" absorption), with a well-defined isosbestic point at 446 nm as the amount of KOH increased from 0 to 4 equivalents (Figure 7 top), indicating that self-assembly of complex **1** becomes more significant as more anionic sites on the polymer are being generated. In line with the electronic absorption studies, an enhancement of the ^{3}MMLCT emission was observed upon excitation at the isosbestic point, and the emission band almost reached the maximum intensity when one equivalent of KOH was used (Figure 7 bottom).

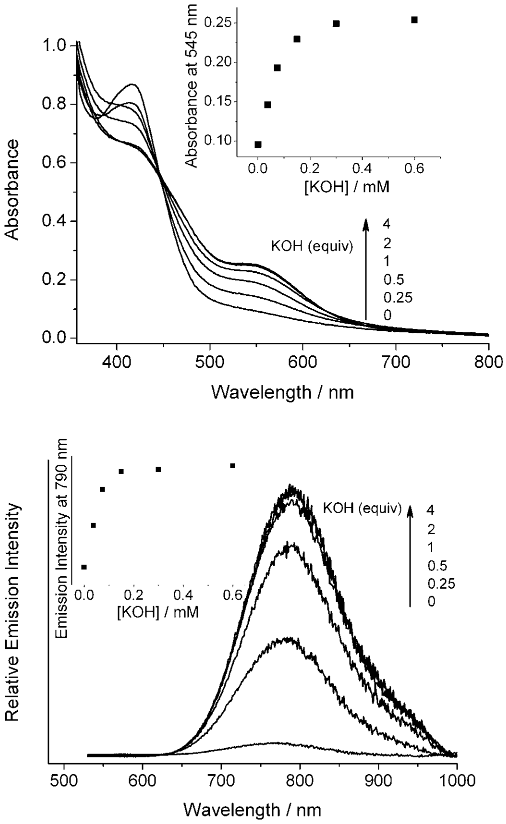


Figure 7. UV/Vis absorption (top) and emission (bottom) changes of complex **1** and polyacetylene in methanol upon addition of 0 to 4 equivalents KOH (concentration of **1** or polyacetylene: 0.15 mM).

Circular dichroism (CD) spectroscopic studies: According to the previous studies,[34–36] the organizational structures of the amphiphilic polyacetylenes can be modulated by changing the external environments such as solvent and pH in the morphological assembling processes; in other words, the high-order chain conformations of the synthetic polyacetylenes could be manipulated by external stimuli. CD spectroscopy is a powerful tool for investigating helical structures in the solution state. The CD spectra of poly(4-ethynylbenzoyl-L-valine) and its analogues in various solvent mixtures, temperature, and KOH concentration were studied previously.[36] In general, the CD spectra of poly(4-ethynylbenzoyl-L-valine) in methanol consisted of a positive band at about 370 nm of moderate intensity, a negative band between about 350 and 292 nm of moderate intensity and another stronger positive band between about 292 and 240 nm. It was also reported that KOH introduction into the polymer would weaken the CD signals due to the interruption of hydrogen bond formation through ionization of the amino acid, and thus the chain helicity could be modulated by pH adjustment as indicated in Figure 3. In this study, similar CD changes of the polyacetylene upon KOH addition were observed, while a CD enhancement took place when platinum(II) complexes were added into the basic mixture under constant ionic strength (Figure 8). It is likely that the addition of the cationic platinum(II) complexes to the random polymer chain would lead to charge neutralization as the cationic platinum(II) complexes would be electrostatically attracted to the anionic sites, reducing the coulombic repulsion between the anionic sites of the polymer. The induced self-assembly of the platinum(II) complexes would

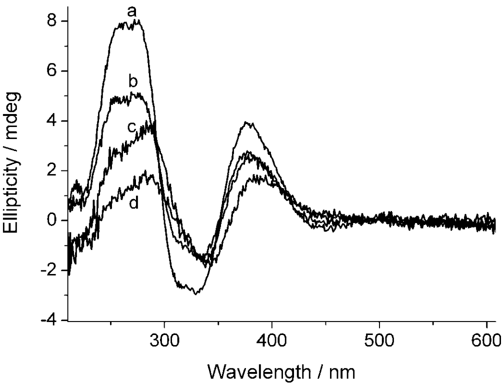


Figure 8. CD spectra in methanol of 0.15 mM polyacetylene (line a), and upon addition of: 0.15 mM complex **1** and 0.15 mM KOH (line b); 0.075 mM complex **1** and 0.15 mM KOH (line c); 0.15 mM KOH (line d).

also provide an additional driving force for the assembly of the polymer chain into helical structures, leading to the revival of the helical chirality. Since no new band formation was found in the CD spectra, the spectral changes observed in the complex–polyacetylene mixture and the mixture with base are believed to mainly originate from electronic transitions characteristic of the polyacetylene. The result of stronger CD intensity with a small shift in the band maximum of the complex/polyacetylene/KOH with respect to the polyacetylene/KOH alone indicates an increase in the chain helicity after the metal complex addition (Figure 3). With reference to our previous studies,[27] CD changes that originate from electronic transitions of the platinum(II) complexes bound to helical biopolymers were found to be broad and in the region of about 300 to 500 nm. The lack of CD signal contribution from the platinum(II) complexes in the present studies may be rationalized by the masking of the high CD intensities of polyacetylene in that region. Nevertheless, the results suggest that introduction of metal complexes could induce or enhance the helical conformation of the polyelectrolyte by metal–polyacetylene electrostatic charge neutralization leading to self-assembly via Pt–Pt and π–π interactions, which stabilizes the chain helicity.

Summary and Prospects

We have demonstrated that a synthetic helical polyacetylene, namely poly(4-ethynylbenzoyl-L-valine), can induce aggregation and self-assembly of alkynylplatinum(II) terpyridyl complexes in common organic solvents upon ionization of the amino acid units under basic conditions. The induced aggregation of the platinum(II) complexes was driven by the electrostatic attraction of the complex molecules to the polyelectrolyte, metal–metal and ligand π–π stacking interactions, which in turn led to remarkable electronic absorption, emission, and CD spectral changes. The reversible interconversion between the aggregated state and monomeric state takes place via alternate addition of bases and acids. The concentration effect of polyacetylene and/or KOH equivalent on the induced complex assembly was studied in detail. An increase in the stability of the chain helicity of the polyacid conformation could be concluded from the significant CD signal enhancement. We envisage that such spectroscopic changes may be exploited for probing conformational and microenvironmental changes in our parallel research work on polymers and biomolecules.

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