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Complexation of Unsaturated Carbon−Carbon Bonds in π-Conjugated Polymers with Transition Metals

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Abstract: The present paper explores the possibility of preparing π-conjugated organometallic polymer hybrid systems based on a poly(*p*-phenylene ethynylene) (PPE) derivative, in which the ethynylene moieties of the polymer are coordinated to platinum(II) centers. The use of the "bifunctional" $[Pt-(\mu\text{-}Cl)Cl(PhCH{=}CH_2)]_2$ (**2**) allows, under appropriate conditions, the formation of three-dimensionally cross-linked, conjugated PPE−platinum(II) networks. The synthesis of $[Pt-(\mu\text{-}Cl)Cl(PhC{\equiv}CPh)]_2$, as a model compound, and a series of model reactions of **2** with diphenylacetylene (**3**) have enabled an NMR study which has revealed a number of equilibria, and suggests a mixed Pt−styrene−acetylene complex as a key structure. As expected, the coordination of Pt markedly influences the photophysical characteristics of the PPE. The photoluminescence is efficiently quenched, and the absorption maximum in the visible regime experiences a hypsochromic shift upon complexation with **2**.

Introduction

In the past two decades, π-conjugated polymers have attracted significant interest, since these materials may combine the processability and outstanding mechanical properties of polymers with the exceptional, readily tailored electronic and optical properties of functional organic molecules.[1] Especially the discoveries of electrically (semi)conducting,[2] nonlinear optical (NLO),[3] and photo- and electroluminescent (PL, EL)[4] polymers have promoted the development of synthesis and processing methods of conjugated polymer materials with unique, field-responsive properties. Among a variety of tools that allow the manipulation of the electronic properties of conjugated macromolecules, the introduction of transition metals into conjugated polymers has recently received considerable attention.[5,6] The latter is promoted by the opportunity to tailor both components of these hybrid systems and the possibility to exploit a diversity of effects, including charge-transfer-, redox-, and energy transfer processes. Of particular attractivity to us is the—to our best knowledge previously never exploited—possibility to complex conjugated polymers with bifunctional metal centers that allow the formation of three-dimensionally cross-linked conjugated structures. Such conjugated networks may overcome the notori-

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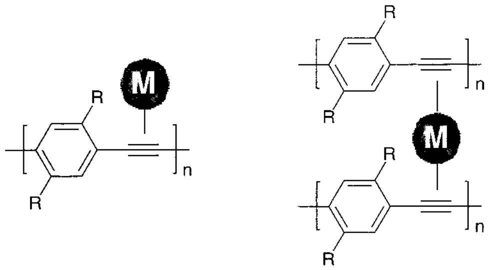

Figure 1. Schematic representation of the π-conjugated organometallic polymers proposed.

ous problems that are usually associated with interchain charge transfer through hopping processes[7] and may be expected to exhibit improved transport characteristics. The latter, in turn, are anticipated to vastly rectify a number of electromagnetic properties and eventually may lead to, for example, increased electrical conductivity and improved nonlinear optical response.

Conventional concepts for the design of π-conjugated organometallic polymers include the formulation of simple blends of metal complexes and a conjugated polymer,[8] as well as the incorporation of metal centers into polymers through coordinative bonds.[6,9−11] In the latter case, the metal atoms may be coordinated to,[9,11] or integrated in, the polymer backbone[6] or alternatively can be attached via conjugated or nonconjugated spacer units in the form of side groups.[10] Among a plethora of functional groups which may serve as ligands for transition metals, we here focus on the utilization of unsaturated (acyclic) carbon−carbon bonds as potential binding sites. These moieties allow the formation of a wide variety of metal complexes that access a broad spectrum of interesting electronic characteristics[12,13] and have also previously been used for the synthesis of organometallic polymer systems; the polymeric silyl acetylene−cobalt−carbonyl complexes introduced by Corriu and coworkers provide a prominent example for the latter.[14] However, the concept of directly employing ethynylene or vinylene moieties for the controlled formation of metal-complexed macromolecules—to our best knowledge—has never been adapted for *π-conjugated* polymers.[15] This is surprising in view of the availability of unsaturated bonds in conjugated polymers,[4] in particular in poly(*p*-phenylene vinylene) (PPV),[16] poly(*p*-phenylene ethynylene) (PPE),[17] and their derivatives, which represent role models of conjugated polymers. Thus, we have embarked on the exploration of the possibility to synthesize and process cross-linked, π-conjugated, organometallic polymer hybrid systems, and here present our initial study on the synthesis and characterization of novel poly(*p*-phenylene ethynylene) platinum(II) complexes (Figure 1).

The conjugated polymer employed in the present work is MEH−OPPE (**7**),[18] a highly soluble poly(2,5-dialkoxy-*p*-phenylene ethynylene) derivative which is representative for a family of conjugated polymers with well-documented PL,[19] EL,[20] and NLO properties,[21] and offers two ethynylene moieties per repeat unit as potential ligand sites (Scheme 3). On the other hand, platinum(II) is well-known to form stable complexes with unsaturated organic ligands.[22] Its square-planar ligand sphere offers the advantage of a restricted number of isomers (when compared to octahedrically coordinated metal centers), and ligand exchange reactions can readily be followed in situ by nuclear magnetic resonance methods, due to the nuclear spin of $^1/_2$ of ^{195}Pt. Concomitantly, we have elected to exemplary employ the dinuclear $[\mathrm{Pt}{-}(\mu\text{-Cl})\mathrm{Cl}(\mathrm{PhCH{=}CH_2})]_2$ (**2**)[22] (Scheme 1) in the present study, assuming that the latter—after ligand exchange—can readily form complexes with the MEH−OPPE's ethynylene moieties. Of particular attractivity, of course, is the "bifunctional" nature of **2**, which we anticipated—and demonstrate—to allow, under appropriate conditions, the formation of three-dimensionally cross-linked, conjugated structures.

Results and Discussion

The dinuclear *sym-trans*-$[\mathrm{Pt}{-}(\mu\text{-Cl})\mathrm{Cl}(\mathrm{PhCH{=}CH_2})]_2$ complex **2** was synthesized from *cis*-dichlorobis(styrene)platinum(II) (**1a**) (Scheme 1) according to a previously published procedure.[22] We should point out also that **1a** might react with the PPE in desirable fashion; however, in contrast to **2** it exhibits only a limited solubility in suitable solvents for the polymer (e.g., $CHCl_3$, toluene). To explore the behavior of *sym-trans*-$[\mathrm{Pt}{-}(\mu\text{-Cl})\mathrm{Cl}(\mathrm{PhCH{=}CH_2})]_2$ in ligand-exchange reactions with molecules containing ethynylene moieties, we first conducted a number of model reactions. First, **2** was treated with an excess of diphenylacetylene in dichloromethane solution, and the reaction product was isolated by precipitation with pentane (Scheme 1). The chemical composition of the product, as determined by organic elemental analysis, is consistent with the dinuclear $[\mathrm{Pt}{-}(\mu\text{-Cl})\mathrm{Cl}(\mathrm{PhC{\equiv}CPh})]_2$ complex **3**. Consistently, the styrene ligands were quantitatively replaced by diphenylacetylene, as is evident from ^{1}H NMR spectroscopy. Free styrene could, indeed, be observed in the supernatant solution after precipitation of **3**, when the reaction was repeated using deuterated solvents. The ^{1}H NMR spectrum of **3** shows a number of well-resolved signals above 8 ppm, which are absent in the case of both educts, and are, also in their magnitude, consistent with the complexation of the diphenylacetylene. The ^{195}Pt NMR spectrum reveals two different platinum signals which we explain with the coexistence of different isomers, for example, the *sym-cis* and *sym-trans* isomer of the dinuclear complex (for simplicity, all complexes occurring in different isomers are represented in their *sym-trans* form in Schemes 1−3). The signals associated with **3** are clearly broader than those of **2**, suggesting that dynamic processes are more pronounced in the former, even at a temperature of 203 K. We should note that **3** was found to slowly decompose in dichloromethane solution, as unequivocally demonstrated by NMR spectra taken after 16 h at room temperature. The ^{195}Pt NMR spectrum of **3** remains essentially unchanged upon addition of an excess (7 equiv) of

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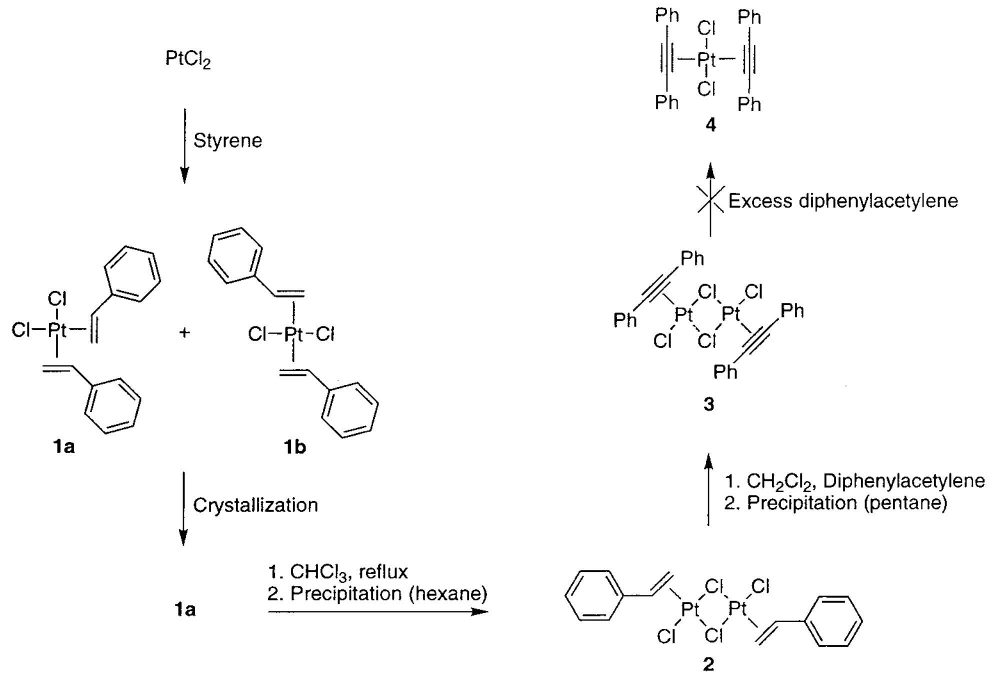
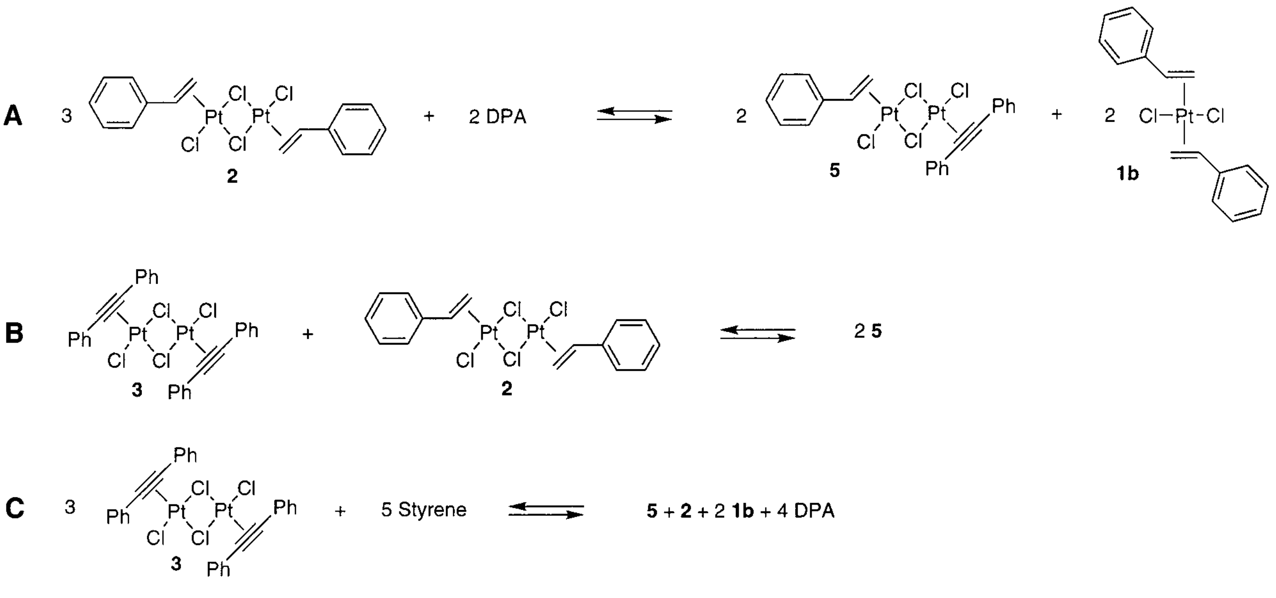
Scheme 1. Synthesis of the Dinuclear Platinum(II) Complex [Pt−(*μ*-Cl)Cl(PhCH=CH$_2$)]$_2$ (**2**) and Model Compound [Pt−(*μ*-Cl)Cl(PhC≡CPh)]$_2$ (**3**)[a]



[a] Note that for simplicity, all complexes occurring in different isomers are represented in their *sym-trans* form.

Scheme 2. Suggested Equilibria (Summarized) for the Reaction of (a) [Pt−(*μ*-Cl)Cl(PhCH=CH$_2$)]$_2$ (**2**) and Diphenylacetylene (DPA), (b) [Pt−(*μ*-Cl)Cl(PhC≡CPh)]$_2$ (**3**), and [Pt−(*μ*-Cl)Cl(PhCH=CH$_2$)]$_2$ (**2**), and (c) [Pt−(*μ*-Cl)Cl(PhC≡CPh)]$_2$ (**3**) and Styrene



diphenylacetylene, suggesting that dichlorobis(diphenylacetylene)platinum(II) (**4**) is not formed in appreciable concentration under the conditions applied (reaction at room temperature for 1 h).

Interestingly, the formation of **3** could not be observed in situ, when *sym-trans*-[Pt−(*μ*-Cl)Cl(PhCH=CH$_2$)]$_2$ (**2**) and diphenylacetylene were combined in dichloromethane under similar conditions as applied for the above-discussed isolation of **3** (Scheme 2a). The ^{1}H NMR spectra of solutions of **2** and diphenylacetylene show a weak signal above 8 ppm, which was found to increase as a function of time (over several hours) and diphenylacetylene concentration and is consistent with the formation of a diphenylacetylene−Pt complex. Importantly, no free styrene could be observed in the ^{1}H NMR spectra, indicating that styrene is a substantially stronger ligand than diphenylacetylene for the complexes investigated here. The ^{195}Pt NMR spectra of these solutions are void of the characteristic signals of **3** but feature a new signal at −2600 ppm, the relative intensity of which also increased as a function of reaction time and diphenylacetylene concentration. At first glance, the four signals associated with **2** (between −2300 and −2420 ppm) are still present, but their relative intensities change significantly, and the signals broaden considerably. The signal at −2600 ppm coincides with the chemical shift of *trans*-dichlorobis(styrene)platinum(II) (**1b**).[23] The facts that diphenylacetylene coordinates to Pt, that no free styrene is observed, and that **1b** seems to be formed suggest an equilibrium reaction according to Scheme

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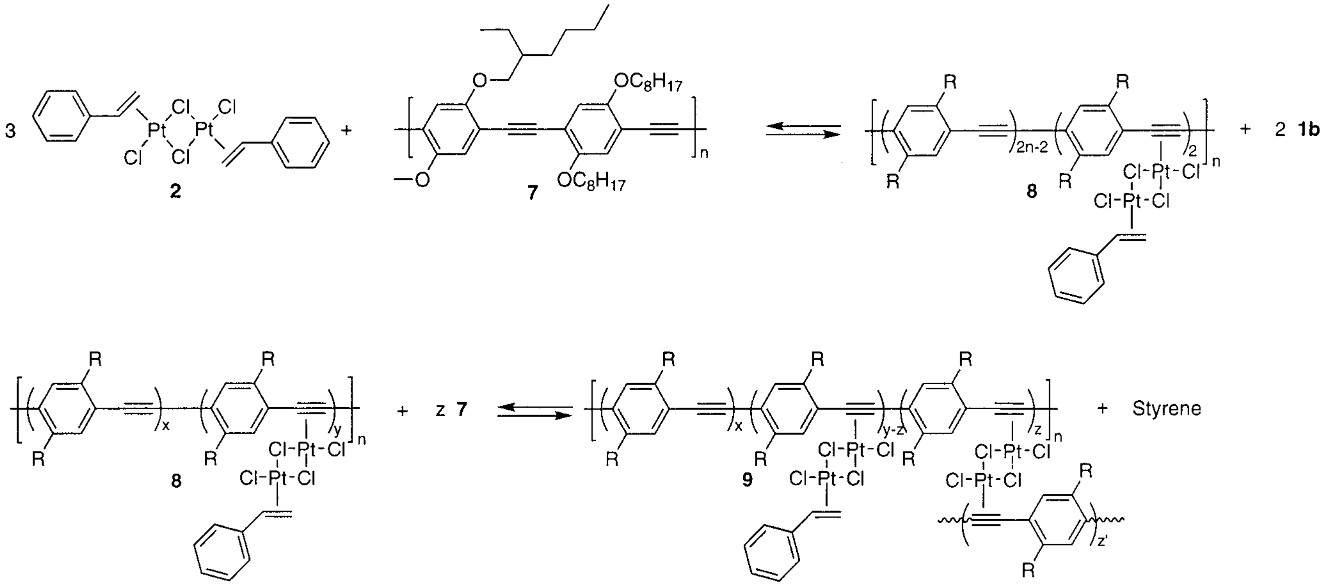
Scheme 3. Suggested Equilibria for the Reaction of [Pt−(μ-Cl)Cl(PhCH=CH$_2$)]$_2$ (**2**) and MEH−OPPE (**7**)



2a under formation of **5**. While the signal related to **1b** clearly appears in the ^{195}Pt NMR spectra, characteristic signals for a new Pt−diphenylacetylene complex are only detected in ^{1}H NMR spectra but in ^{195}Pt NMR spectra appear to broadly overlap with the signals of **2**.

To obtain further proof for this interpretation, we have also investigated the ligand-exchange reaction between **2** and **3** (Scheme 2b). As expected, the formation of **1b** is not observed in this case, while the signals of **3** are still present, and again, the relative intensities and width of the signals in the region between −2300 and −2420 ppm change as above, suggesting again the formation of **5**. In another experiment, we have finally investigated the addition of styrene to **3** (Scheme 2c). In agreement with the above observations on the relative complexing strength of styrene and diphenylacetylene, ^{195}Pt and ^{1}H NMR spectra show that the addition of about 2 equiv of styrene to **3** leads to the disappearance of **3**, and the observed signals are consistent with the formation of **2**, **5**, and **1b** (cf. Scheme 2c); if, however, an excess of styrene was added, only **1b** could be detected. We should note that in none of the systems described above was evidence for the presence of the mononuclear complex dichloro(diphenylacetylene)(styrene)platinum(II) obtained, but we can also not entirely exclude its presence.

The above model reactions imply that the bis(diphenylacetylene) complex **3** is only obtained under kinetically controlled conditions. Therefore, **2** should be an extremely suitable candidate for the preparation of three-dimensionally cross-linked, conjugated polymer−Pt complexes as outlined in Figure 1 and Scheme 3. The results suggest that in dilute solutions containing **2** and MEH−OPPE, styrene is only partially replaced, cross-linking is essentially prevented, and thus, the reaction products should remain dissolved. This is, of course, of vital importance for the processability of such systems (cf. below).

In analogy to the above model experiments, we have studied the in situ complexation of MEH−OPPE (**7**) and **2** (Scheme 3), in trichloromethane/dichloromethane mixtures employing **7**:**2** weight-ratios between 0 and 3.25, corresponding to molar ratios between 0 and 4.7 (calculations are always based on the molecular weight of the PPE's repeat unit). Gratifyingly, all mixtures remained completely soluble, and as a matter of fact, ^{1}H NMR and ^{195}Pt NMR data reflect a similar behavior for the complexation of **7** and **2** as discussed above for the low-molecular **2**/diphenylacetylene model system. The ^{195}Pt NMR spectra of these solutions feature a signal at −2607 ppm which is attributed to **1b**, the relative intensity of which increased as a function of PPE concentration. In addition, the four signals associated with **2** (between −2300 and −2420 ppm) broaden considerably if the PPE is added, as was previously observed for the low-molecular-weight model system. Thus, based on the striking analogy to the model system, we surmise that the complexation of MEH−OPPE (**7**) with **2** (Scheme 3) under the presently employed conditions leads to the formation of mixed complexes **8**.

The photophysical characteristics of these Pt−PPE hybrids were investigated by steady-state photoluminescence and UV−vis absorption measurements. The absorption and emission spectra obtained for deoxygenated trichloromethane solutions are shown in Figure 2; note that the **2**:**7** ratios were in the same range as those used for the in situ NMR experiments (**2**:**7** molar ratios between 0 and 5), but due to the high extinction coefficient of **7**, the absolute concentrations had to be chosen about 50 000 times lower for the optical experiments. Figure 2a clearly shows that the addition of **2** induces a dramatic reduction in PL intensity, while the shape of the emission spectrum remains essentially unchanged. As expected, the PL quenching was observed to correlate with the concentration of **2**, and the emission was virtually entirely suppressed in the case of a **2**:**7** ratio of 5. This behavior is fully consistent with the formation of complexes **8** according to Scheme 3, with exciton migration along the polymer main chains to the complexation sites, which seem to represent low-energy states and provide pathways for nonemissive relaxation processes. Figure 2b shows that the absorption spectra are also affected by addition of **2**; however, the effect is less pronounced at low concentrations of **2**. The observed hypsochromic shift of the absorption band and the reduction of the extinction coefficient reflect that the electronic properties of the backbone itself also are affected through the complexation, and one could speculate that the effective conjugation length is reduced. To rule out that the observed PL quenching originates from Förster-type energy transfer between noncomplexed species, we have conducted comparative experiments with platinum complexes which feature strongly bound ligands that are not expected to be replaced by the acetylenic moieties. Gratifyingly, the photophysical characteristics of

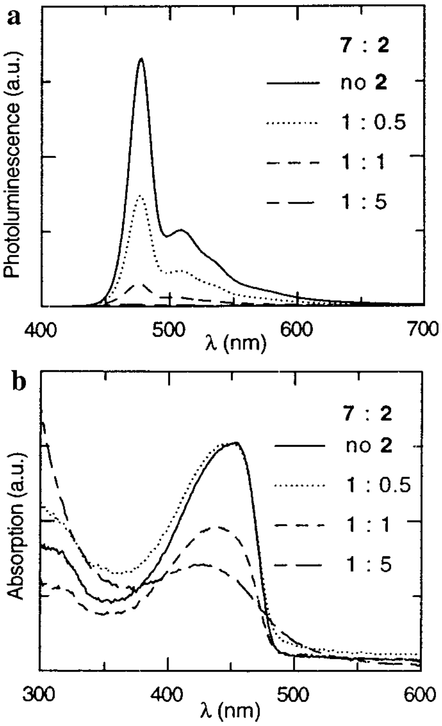


Figure 2. Photoluminescence (a) and UV−vis absorption spectra (b) of solutions of MEH−OPPE (**7**) ($5 \cdot 10^{-7}$ g·mL^{-1}) and [Pt−(μ-Cl)Cl(PhCH═CH$_2$)]$_2$ (**2**) in CHCl$_3$. The figures show the influence of the concentration of **2**, which is given in molar equivalents with respect to the MEH−OPPE's repeat unit.

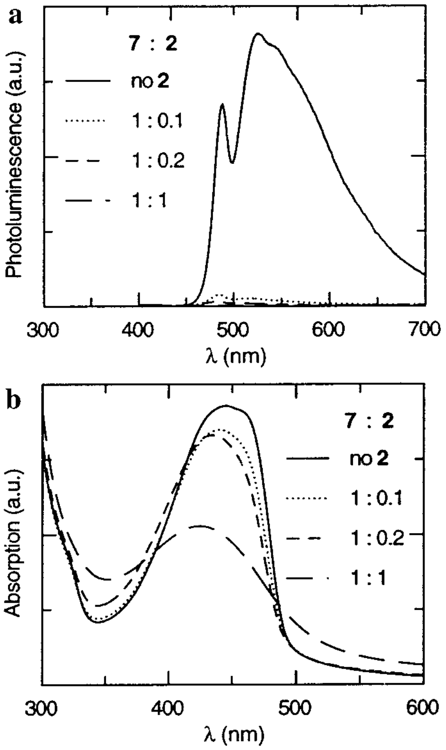


Figure 3. Photoluminescence (a) and UV−vis absorption spectra (b) of spin-cast films of MEH−OPPE (**7**) and [Pt−(μ-Cl)Cl(PhCH═CH$_2$)]$_2$ (**2**). The figures show the influence of the concentration of **2**, which is given in molar equivalents with respect to the MEH−OPPE's repeat unit.

solutions of the PPE **7** were found to remain unchanged upon addition of bis(2,5-pentanedionato)platinum(II) or 1,5-cyclooctadienedimethylplatinum(II) (molar ratio of Pt-complex:**7** of 1).

Pt/MEH−OPPE films of good optical quality were prepared by spin coating of trichloromethane solutions comprising **2** and **7** at molar ratios between 0 and 1 (see Experimental Section for details). Important for the preparation of these films is the fact that Pt/MEH−OPPE solutions of homogeneous appearance could be prepared at polymer concentrations useful for this processing method (10 mg·mL^{-1}) if MEH−OPPE of a number-average molecular weight of about 8100 g·mol^{-1} was employed. Interestingly, once the films had been prepared, they were found to be insoluble in trichloromethane and toluene, indicating that indeed cross-linking complexes (i.e., **9**, $z > 0$) as shown in Scheme 3 were formed. In agreement, the Pt-containing films could readily be released from the substrate and exhibited mechanical properties that allowed them to be easily handled in free-standing form, very much in contrast to untreated MEH−OPPE films which, due to the PPE's low molecular weight, were extremely brittle. The insolubility of these films in the solvent of their origin could simply be a kinetic phenomenon, but may also be an indication that styrene has evaporated during processing and, therefore, has been withdrawn from the equilibrium. The fact that the addition of styrene to the solvent was found to readily dissolve the films and restored the photoluminescence of the released PPE strongly supports the latter prospect and shows that the Pt−PPE complexation is indeed reversible. In view of the extreme sensitivity of the PPE's PL characteristics toward complexation with Pt(II) (Figure 2a) and the expected hypsochromic shift of the PL emission band upon chain-scission, the observed restoration of the PPE's PL seems to suggest that the PPE has been essentially re-converted to its original form. IR spectra of films containing **2** and **7** at molar ratios of 0.1 and 1, respectively, show besides the characteristic signals of **7** also appreciable signals due to coordinated styrene, which besides **9** indicate the presence of **2** or mixed styrene acetylene complexes (e.g. **8**).

The absorption and emission spectra of the Pt/MEH−OPPE films produced are shown in Figure 3. The observed changes in their photophysical characteristics as a function of the amount of **2** added are qualitatively similar to those of the solutions. However, Figure 3a demonstrates that already the presence of minute amounts of **2** leads to an essentially complete quenching of the PL emission. Of course, this behavior reflects again a pronounced shift of the equilibrium outlined in Scheme 3 in the solid state and indicates substantial coordination of the Pt already at low concentrations of **2**. Also in the case of films, we have conducted comparative experiments using PPE (**7**) and bis(2,5-pentanedionato)platinum(II) (molar ratio of 1). The PL spectrum of the latter, Pt-containing film perfectly matches the one of the neat PPE, indicating that even in this dense, highly Pt-loaded system, the electronic interactions between the PPE and the Pt complex are negligible and that coordination between Pt and PPE moieties is indeed required to substantially influence the optical characteristics of the conjugated polymer system.

Conclusions

In summary, we have shown with the example of poly(*p*-phenylene ethynylene) that the ethynylene moieties comprised in π-conjugated polymers can readily coordinate to platinum(II) in exchange with weakly bound ligands. The "bifunctional" [Pt−(μ-Cl)Cl(PhCH═CH$_2$)]$_2$ employed in the present study, under appropriate conditions, allows the formation of three-dimensionally cross-linked, conjugated PPE−Pt networks. Importantly, in dilute solutions, the equilibrium of the presently investigated PPE−Pt systems dictates non-crosslinked structures, and the system remains homogeneous and therewith processable.

As expected, the coordination of Pt markedly influences the photophysical characteristics of the PPE. After having employed $[Pt-(\mu\text{-}Cl)Cl(PhCH{=}CH_2)]_2$ in the present study to demonstrate the possibility of preparing a new family of π-conjugated organometallic polymer hybrid systems, we envision the extension of the present concepts to the use of metal complexes with specific PL characteristics and the conduction of experiments related to the charge-carrier transport in such cross-linked π-conjugated polymer systems.

Experimental Section

Materials and Methods. All reagents and solvents were of analytical grade quality, were purchased from Aldrich Chemical Co. or Fluka, and were used without further purification. *cis*-Dichlorobis(styrene)-platinum(II) (**1**),[22] *sym-trans*-$[Pt-(\mu\text{-}Cl)Cl(PhCH{=}CH_2)]_2$ (**2**),[22] and MEH−OPPE (**7**)[18] of a number-average molecular weight of 8100 $g{\cdot}mol^{-1}$ were prepared as described before. ^1H NMR and ^{195}Pt NMR spectral data were obtained in CD_2Cl_2 or $CDCl_3$ or mixtures of these solvents on a Bruker 300 MHz NMR spectrometer and are expressed in ppm relative to tetramethylsilane (^1H) and sodium hexachloroplatinate(IV) (^{195}Pt), respectively. IR spectra were recorded on KBr substrates on a Bruker IFS 66v. Elemental analyses were carried out by the Microanalysis Laboratory of the Laboratory of Organic Chemistry of ETH Zürich. UV−vis absorption spectra were obtained on a Perkin-Elmer Lambda 900. PL spectra were measured under excitation at 380 nm on a SPEX Fluorolog 3 (model FL3-12). Corrections for the spectral dispersion of the Xe-lamp, the instrument throughput, and the detector response were applied.

NMR Spectra of *sym-trans*-$[Pt-(\mu\text{-}Cl)Cl(PhCH{=}CH_2)]_2$ (2). For the purpose of internal reference, NMR spectra of **2** were recorded. ^1H NMR (300 MHz, CD_2Cl_2, 203 K) δ 7.55−7.28 (3 × m, 10 H, ar), 6.50 (m br, 2 H, $C{=}CH$), 5.15−4.40 (m, 4 H, $C{=}CH_2$); ^1H NMR (300 MHz, CD_2Cl_2, 300 K) δ 7.75−7.50 (m, 6 H, ar), 7.49−7.30 (m, 4 H, ar), 6.55 (m br, 2 H, $C{=}CH$), 5.13 (m br, 2 H, $C{=}CH_2$), 4.78 (m, 2 H, $C{=}CH_2$); ^{195}Pt NMR (64 MHz, CD_2Cl_2, 203 K) δ −2306, −2321, −2331, −2415; ^{195}Pt NMR (64 MHz, CD_2Cl_2, 300 K) δ −2306, −2321, −2331, −2415.

Synthesis of $[Pt-(\mu\text{-}Cl)Cl(PhC{\equiv}CPh)]_2$ (3). *sym-trans*-$[Pt-(\mu\text{-}Cl)Cl(PhCH{=}CH_2)]_2$ (**2**) (433 mg, 0.588 mmol) was dissolved in CH_2Cl_2 (24 mL), the solution was filtered, and diphenylacetylene (2.47 g, 13.9 mmol) was added. The reaction mixture was stirred for 5 min at room temperature, and pentane (220 mL) was added, causing the immediate precipitation of the product. The suspension was allowed to stand for 30 min, and the solid was filtered off, washed with pentane (30 mL), and dried in vacuo. Reprecipitation from dichloromethane/pentane (30/85 mL) followed by drying in vacuo afforded 218 mg (0.246 mmol, 42%) of a brown solid. ^1H NMR (300 MHz, CD_2Cl_2, 213 K) δ 8.47−8.01 (m, ∼4 H, ar ortho to $C{\equiv}C$ and facing Pt), 7.98−6.89 (m, ∼16 H, other ar), ^{195}Pt NMR (64 MHz, CD_2Cl_2, 213 K) δ −1610 (weak), −1868, −1926. Anal. Calcd for $C_{28}H_{20}Cl_4Pt_2$: C, 37.85; H, 2.27; Cl, 15.96. Found: C, 37.38; H, 2.53; Cl, 15.12.

Investigation of the Ligand-Exchange Reaction between $[Pt-(\mu\text{-}Cl)Cl(PhC{\equiv}CPh)]_2$ (3) and Diphenylacetylene. In an NMR tube, $[Pt-(\mu\text{-}Cl)Cl(PhC{\equiv}CPh)]_2$ (**3**) (10 mg, 0.011 mmol) was dissolved in CD_2Cl_2 (0.75 mL), and diphenylacetylene (172 mg, 0.079 mmol) was added. The solution was kept at room temperature, and NMR spectra were recorded about 10 min and 1 h, respectively, after mixing. After 10 min: ^{195}Pt NMR (64 MHz, CD_2Cl_2, 223 K) δ −1867, −1926, −2537 (weak). After 1 h:^{195}Pt NMR (64 MHz, CD_2Cl_2, 223 K) δ −1867, −1926, −2207 (weak), −2537 (weak).

Investigation of the Ligand-Exchange Reaction between *sym-trans*-$[Pt-(\mu\text{-}Cl)Cl(PhCH{=}CH_2)]_2$ (2) and Diphenylacetylene. In an NMR tube, *sym-trans*-$[Pt-(\mu\text{-}Cl)Cl(PhCH{=}CH_2)]_2$ (**2**) (10 mg, 0.014 mmol) was dissolved in CD_2Cl_2 (0.75 mL), and diphenylacetylene (4.5 mg, 0.025 mmol) was added. The solution was kept at room temperature, and NMR spectra were recorded about 10 min, 1 h, and 18 h, respectively, after mixing. After 10 min:^1H NMR (300 MHz, CD_2Cl_2, 203 K) δ 8.10 (m br, ∼0.2 H, coordinated diphenylacetylene), 7.55 (m, ∼14 H, ar), 7.38 (m, ∼16 H, ar), 6.50 (m, 2 H, $C{=}CH$), 5.15 (m br, 2 H, $C{=}CH_2$), 4.82 (m, 2 H, $C{=}CH_2$); ^{195}Pt NMR (64 MHz, CD_2Cl_2, 203 K) δ −2306, −2320, −2331, −2414, −2600 (weak). After 1 h: ^1H NMR (300 MHz, CD_2Cl_2, 203 K) δ 8.10 (m br, ∼0.2 H, coordinated diphenylacetylene), 7.55 (m, ∼14 H, ar), 7.40 (m, ∼16 H, ar), 6.50 (m, 2 H, $C{=}CH$), 5.15 (m br, 2 H, $C{=}CH_2$), 4.82 (m, 2 H, $C{=}CH_2$); ^{195}Pt NMR (64 MHz, CD_2Cl_2, 203 K) δ −2306, −2320, −2331, −2414, −2600 (weak). After 18 h: ^1H NMR (300 MHz, CD_2Cl_2, 203 K) δ 8.10 (m br, ∼0.2 H, coordinated diphenylacetylene), 7.55 (m, ∼14 H, ar), 7.40 (m, ∼16 H, ar), 6.50 (m, 2 H, $C{=}CH$), 5.15 (m br, 2 H, $C{=}CH_2$), 4.82 (m, 2 H, $C{=}CH_2$); ^{195}Pt NMR (64 MHz, CD_2Cl_2, 203 K) δ −2306, −2320, −2331, −2413, −2600.

The above experiment was repeated with 86 mg instead of 4.5 mg of diphenylacetylene and NMR spectra were recorded about 10 min, 1 h, and 18 h, respectively, after mixing. After 10 min: ^1H NMR (300 MHz, CD_2Cl_2, 203 K) δ 8.10 (m br, ∼1.3 H, coordinated diphenylacetylene), 8.00−7.05 (m, ∼300 H, ar), 6.50 (m, 2 H, $C{=}CH$), 5.15 (m br, 2 H, $C{=}CH_2$), 4.82 (m, 2 H, $C{=}CH_2$); ^{195}Pt NMR (64 MHz, CD_2Cl_2, 203 K) δ −2305, −2320, −2328, −2412, −2601. After 1 h: ^1H NMR (300 MHz, CD_2Cl_2, 203 K) δ 8.10 (m br, ∼2 H, coordinated diphenylacetylene), 8.00−7.05 (m, ∼300 H, ar), 6.50 (m, 2 H, $C{=}CH$), 5.15 (m br, 2 H, $C{=}CH_2$), 4.82 (m, 2 H, $C{=}CH_2$); ^{195}Pt NMR (64 MHz, CD_2Cl_2, 203 K) δ −2305, −2320, −2328, −2412, −2601. After 18 h: Multitudes of signals indicate decomposition of the complex.

In an NMR tube, *sym-trans*-$[Pt-(\mu\text{-}Cl)Cl(PhCH{=}CH_2)]_2$ (**2**) (20 mg, 0.028 mmol) was dissolved in CD_2Cl_2 (0.75 mL), and diphenylacetylene (172 mg, 0.97 mmol) was added. The solution was kept at room temperature, and an excess cyclohexane-d_{12} was added, causing the immediate precipitation of a solid. The latter was isolated by centrifugation and decantation of the supernatant solution, and NMR spectra of solid and supernatant solution were immediately recorded. Supernatant solution: ^1H NMR (300 MHz, CD_2Cl_2, 203 K) δ 7.60−7.00 (m, excess diphenylacetylene), 6.61 (d × d, 1 H, $C{=}CH$), 5.60 (d, 1 H, $C{=}CH_2$, J = 17.0 Hz), 5.08 (d, 1 H, $C{=}CH_2$, J = 11.3 Hz), 1.40 (m, excess cyclohexane-d_{12}). Solid: ^{195}Pt NMR (64 MHz, CD_2Cl_2, 203 K) δ −1871, −1932.

Investigation of the Ligand-Exchange Reaction between *sym-trans*-$[Pt-(\mu\text{-}Cl)Cl(PhCH{=}CH_2)]_2$ (2) and $[Pt-(\mu\text{-}Cl)Cl(PhC{\equiv}CPh)]_2$ (3). In an NMR tube, *sym-trans*-$[Pt-(\mu\text{-}Cl)Cl(PhCH{=}CH_2)]_2$ (**2**) (10 mg, 0.014 mmol) was dissolved in CD_2Cl_2 (0.75 mL), and $[Pt-(\mu\text{-}Cl)Cl(PhC{\equiv}CPh)]_2$ (**3**) (12 mg, 0.014 mmol) was added. The solution was kept at room temperature, and NMR spectra were recorded about 10 min and 5 h, respectively, after mixing. After 10 min: ^{195}Pt NMR (64 MHz, CD_2Cl_2, 213 K) δ −1610 (weak), −1888, −1912, −2303, −2317, −2326, −2409. After 5 h:^{195}Pt NMR (64 MHz, CD_2Cl_2, 213 K) δ −1888, −1912, −2303, −2317, −2326, −2409.

Investigation of the Ligand-Exchange Reaction between $[Pt-(\mu\text{-}Cl)Cl(PhC{\equiv}CPh)]_2$ (3) and Styrene. In an NMR tube, $[Pt-(\mu\text{-}Cl)Cl(PhC{\equiv}CPh)]_2$ (**3**) (7.1 mg, 0.008 mmol) was dissolved in CD_2Cl_2 (0.75 mL), and styrene (1.8 μL, 0.016 mmol) was added. The solution was kept at room temperature, and NMR spectra were recorded about 10 min after mixing. ^1H NMR (300 MHz, CD_2Cl_2, 203 K) δ 8.03 (m br, ∼1 H, coordinated diphenylacetylene), 7.55 (m, ∼12 H, ar), 7.40 (m, ∼18 H, ar), 6.50 (m, 2 H, $C{=}CH$), 5.15−4.80 (m br, 4 H, $C{=}CH_2$); ^{195}Pt NMR (64 MHz, CD_2Cl_2, 203 K) δ −2321, 2332, −2413, −2600.

The above experiment was repeated with 11.8 μL instead of 1.8 μL of styrene. The solution was kept at room temperature, and NMR spectra were recorded about 10 min after mixing. ^{195}Pt NMR (64 MHz, CD_2Cl_2, 223 K) δ −2604.

NMR Experiments on Pt/MEH−OPPE Solutions. ^1H NMR and ^{195}Pt NMR experiments were conducted at 203 K on a sample which originally contained 20 mg of *sym-trans*-$[Pt-(\mu\text{-}Cl)Cl(PhCH{=}CH_2)]_2$ (**2**) in a mixture of CD_2Cl_2 and $CHCl_3$ (2:1 v/v) and to which 10, 20, or 65 mg of MEH−OPPE (**7**) were added. 20 mg **2**/0 mg **7**: ^1H NMR 7.61−7.33 (m, 10 H, ar styrene), 6.56 (m, 2 H, $={CH}$ styrene), 5.25−4.75 (m, 4 H, $={CH_2}$ styrene); ^{195}Pt NMR −2304, −2327, −2329, −2412. 20 mg **2**/10 mg **7**: ^1H NMR 7.61−7.34 (m, 10 H, ar styrene), 7.12−7.01 (m, 2 H, ar MEH−OPPE), 6.56 (m, 2 H, $={CH}$ styrene), 5.21−4.89 (m, 4 H, $={CH_2}$ styrene), 3.96 (m, 5 H, OCH_3 and OCH_2 MEH−OPPE), 1.91 (m, 1 H, CH MEH−OPPE), 1.52−1.33 (m, 8 H, 4 × CH_2 MEH−OPPE), 0.99 (s, 3 H, CH_3 MEH−OPPE), 0.91 (s, 3 H, CH_3 MEH−OPPE); ^{195}Pt NMR −2304, −2329, −2412, −2607. 20 mg **2**/20 mg **7**: ^{1}H NMR 7.59−7.34 (m, 10 H, ar styrene), 7.12−7.01 (m, 2 H, ar MEH−OPPE), 6.56 (m, 2 H, ═CH styrene), 5.21−4.88 (m, 4 H, ═CH_2 styrene), 3.96 (m, 5 H, OCH_3 and OCH_2 MEH−OPPE), 1.91 (m, 1 H, CH MEH−OPPE), 1.53−1.34 (m, 8 H, 4 × CH_2 MEH−OPPE), 0.99 (s, 3 H, CH_3 MEH−OPPE), 0.91 (s, 3 H, CH_3 MEH−OPPE); ^{195}Pt NMR −2304, −2328, −2412, −2607. 20 mg **2**/65 mg **7**: ^{1}H NMR 7.56−7.42 (m, 10 H, ar styrene), 7.12−7.01 (m, 2 H, ar MEH−OPPE), 6.56 (m, ∼2 H, ═CH styrene), 5.21−4.88 (m, ∼4 H, ═CH_2 styrene), 3.95 (m, 5 H, OCH_3 and OCH_2 MEH−OPPE), 1.90 (m, 1 H, CH MEH−OPPE), 1.52−1.33 (m, 8 H, 4 × CH_2 MEH−OPPE), 0.95 (m, 6 H, 2 × CH_3 MEH−OPPE); ^{195}Pt NMR −2304, −2326, −2410, −2607.

Photophysical Experiments on Pt/MEH−OPPE Solutions. For all UV−vis absorption and emission experiments in solution, spectroscopic grade $CHCl_3$ was used, and the concentration of MEH−OPPE was kept at $5 \cdot 10^{-7}$ g·mL^{-1}. The solutions were prepared by adding a selected amount (cf. Figure 2) of $[Pt-(\mu\text{-}Cl)Cl(PhCH{=}CH_2)]_2$ (**2**), bis(2,5-pentanedionato)platinum(II), or 1,5-cyclooctadienedimethylplatinum(II) to an aliquot of a MEH−OPPE/$CHCl_3$ solution and deoxygenating the sample by sparging with Ar for 15 min prior to use.

Film Preparation. For the preparation of Pt/MEH−OPPE films, MEH−OPPE was first dissolved in $CHCl_3$ at a concentration of about 8.3×10^{-3} g·mL^{-1}. A selected amount of $[Pt-(\mu\text{-}Cl)Cl(PhCH{=}CH_2)]_2$ (**2**) or bis(2,5-pentanedionato)platinum(II) was added to the MEH−OPPE/$CHCl_3$ solution. Immediately after dissolution of the metal complex, the solutions were filtered through a 0.2 μm filter (Gelman Acrodisc PTFE) and were spin-cast (1000 rpm/15 s) onto fused silica substrates. The polymer films were dried under vacuum at room temperature and in the dark.

For IR spectra, films were prepared by drop casting the above solutions on KBr-pellets and drying under vacuum at room temperature and in the dark. Position of selected IR signals (in cm^{-1}): Film of **2**:**7** molar ratio of 1: 3074 (styrene C−H st), 3054 (styrene C−H st), 3024 (styrene C−H st), 2952 (diphenylacetylene C−H st), 2873 (diphenylacetylene C−H st), 2861 (diphenylacetylene C−H st), 1600 (styrene C═C aryl st), 1202 (diphenylacetylene), 1034 (diphenylacetylene), 862 (diphenylacetylene), 780 (diphenylacetylene), 753 (styrene), 689 (styrene). Film of **2**:**7** molar ratio of 0.1: identical peak positions, lower relative intensity of the signals originating from styrene.

Photophysical Experiments on Pt/MEH−OPPE Films. Emission studies on polymer films were performed in air. The samples were positioned normal to the incident beam, and the emission was detected at an angle of 22.5 ° from the incident beam.

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