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Synthesis and Properties of Metallo-Supramolecular Poly(*p*-phenylene ethynylene)s

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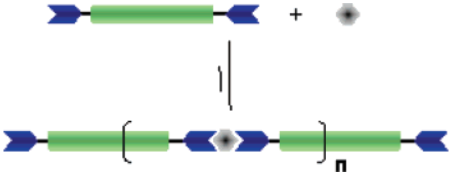
ABSTRACT: The use of metal−ligand binding as the driving force for the self-assembly polymerizations of a ditopic monomer offers a facile route to the preparation of metallo-supramolecular polymers. We report, herein, the utilization of this approach for the polymerization of a conjugated macromonomer that was derived by functionalizing a low-molecular-weight poly(2,5-dialkoxy-*p*-phenylene ethynylene) core with 2,6-bis(1′-methyl-benzimidazolyl)pyridine (Mebip) ligands on the two terminal positions. The supramolecular polymerization of this macromonomer with equimolar amounts of Zn^{2+} or Fe^{2+} resulted in polymers, which exhibit appreciable mechanical strength, but due to their self-assembly ability offer the ease of processing of low-molecular-weight compounds. The optical and thermomechanical properties of the new materials were investigated by a variety of analytical techniques, including ultraviolet−visible and photoluminescence spectroscopy, dynamic mechanical thermoanalysis, and thermogravimetric analysis.

Introduction

Since the discovery of electrical conductivity in π-conjugated polymers three decades ago,[1] (semi)conducting polymers have become the focus of major research and development activities around the globe.[2] The excitement for this new generation of polymeric materials reflects their potential to combine the processability and outstanding properties of polymers with the exceptional, readily tailored electronic and optical properties of functional organic molecules. Especially their potential utilization as synthetic metals[3] and as organic semiconductors in light-emitting diodes,[4] field-effect transistors,[5] photovoltaic cells,[6] sensors,[7] and other devices have motivated the development of synthesis and processing methods of conjugated polymers with unique electronic properties. Unfortunately, high-molecular-weight conjugated polymers typically display high thermal transition temperatures, limited solubility, and high solution viscosity, and processing of these materials is therefore often intricate and time-consuming.[8] Furthermore, it is sometimes difficult to avoid structural defects in these macromolecules and/or to appropriately purify the materials, and hence, defective sequences disrupting the conjugation are not uncommon.[9] Low-molecular-weight conjugated polymers or oligomers are therefore frequently employed,[10] but these materials lack of chain entanglements preventing the expression of “typical polymer properties”.[11] As a result, the mechanical properties of these semiconductors are inferior compared to conventional plastics. The framework of dynamic (reversible) polymerization may represent an attractive approach to solve this dilemma, since it allows one to assemble high-molecular-weight macromolecules from well-defined, easy-to-process precursors.[12] Indeed, several recent studies have reported the successful use of various types of noncovalent interactions for the assembly of conjugated monomers or oligomers.[13] One potentially interesting means of preparing supramolecular polymers of conjugated systems is the utilization of metal−ligand interactions (Scheme 1).[14−18]

Scheme 1. Schematic Representation of the Metallo-Supramolecular Polymerization of Ditopic Ligands



A wide variety of metal−ligand binding motifs is available that offer a broad range of electronic interactions as well as binding characteristics (thermodynamic and kinetic stabilities, etc.),[19] which in turn can be utilized to tune the nature of the resulting supramolecular materials.[20] Interestingly, however, metallo-supramolecular conjugated polymers for which appreciable mechanical properties have been reported appear to be rare. Addressing specifically the mechanical aspects of conjugated self-assembled systems, we report herein the synthesis of metallo-supramolecular poly(*p*-phenylene ethynylene)s (PPEs) and demonstrate that these materials can be readily processed into mechanically stable films and fibers. Guided by our preliminary work that involved a small-molecule ditopic ligand,[21] we chose as building blocks for the supramolecular polymers investigated here: (i) a low-molecular-weight poly(2,5-dialkoxy-*p*-phenylene ethynylene), which is representative for a family of conjugated polymers with well-known optoelectronic properties;[22] (ii) the 2,6-bis(1′-methylbenzimidazolyl)pyridine (Mebip) ligand[23] as the binding unit, which has been previously shown to be a useful metal ion binding motif in the self-assembly of supramolecular polymers;[24] and (iii) Zn^{2+} and Fe^{2+} as two examples of metals which display sufficiently large binding constants with Mebip and offer quite different electronic configuration and characteristics.[21,24]

Experimental Section

General Methods. NMR spectra were recorded on a Varian 300 or 600 MHz NMR spectrometer. Gel permeation chromatography (GPC) data were calibrated against polystyrene standards and collected on a Varian Prostar equipped with a model 350 RI detector and a PSS SDV linear M column with THF as an eluent. Dynamic mechanical thermoanalysis (DMTA) measurements were taken on a Triton Technology Tritec 2000 DMA performing single frequency/

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strain tension (1 Hz, 0.02 mm) experiments on rectangular films at a heating rate of 3 °C/min. Thermogravimetric analysis (TGA) was carried out on a TA Instruments TGAQ500 under N_2 at a heating rate of 20 °C/min. Ultraviolet−visible (UV−vis) absorption spectra were obtained on a Perkin-Elmer Lambda 800 spectrometer. Steady-state photoluminescence (PL) spectra were acquired on a PTI C720 fluorescence spectrometer. Spectra were collected under excitation at 400 nm and are corrected for the instrument throughput and the detector response. Solid-state absorption and PL spectra were measured on spin-cast films.

Materials. 1,4-Dioctyloxy-2,5-diiodobenzene (**1**),[25] 1,4-diethynyl-2,5-bis(octyloxy)benzene (**2**),[25] and 2,6-bis(1′-methylbenzimidazoyl)-4-bromopyridine were prepared according to literature procedures. Unless otherwise stated, all other reagents, solvents, metal complexes, and catalysts were purchased from Aldrich Chemical Co., Fisher Scientific, or Strem Chemicals and were used without further purification. Spectroscopic grade $CHCl_3$ (passed through a plug of basic alumina), spectroscopic grade CH_3CN (Aldrich), and distilled methanol were employed for the optical absorption and emission experiments as well as for the metallopolymerization reactions. THF was distilled from sodium/benzophenone. Toluene, diisopropylamine, and triethylamine were distilled from CaH_2 under an inert atmosphere.

2,6-Bis(1′-methylbenzimidazoyl)-4-(trimethylsilylethynyl)pyridine. To a round-bottom flask containing 2,6-bis(1′-methylbenzimidazoyl)-4-bromopyridine (1.0 g, 2.4 mmol), 5.0% $(PPh_3)_2PdCl_2$ (84 mg, 0.12 mmol), 5% CuI (22 mg, 0.12 mmol), triethylamine (14 mL), and DMF (11 mL) were added, and the mixture was purged with nitrogen for 30 min. Upon heating to 55 °C under stirring, trimethylsilylacetylene (0.85 mL, 5.9 mmol) was added dropwise to the reaction. After 1 h, the reaction mixture was poured hot into a saturated aqueous EDTA solution (100 mL), and the mixture was stirred for 1 h. The organic layer was separated and the aqueous layer extracted with $CHCl_3$. The combined organic layers were washed with deionized water, dried over anhydrous Na_2SO_4, reduced in vacuo, and purified by column chromatography (silica gel, $CHCl_3$) to yield the title compound as an off-white solid (1.0 g, 2.3 mmol, 96%). ^1H NMR (300 MHz, $CDCl_3$): δ 8.43 (s, 2 H), 7.83−7.80 (m, 4 H), 7.35−7.29 (m, 4 H), 4.14 (s, 6 H), 0.28 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.6, 149.4, 142.5, 137.1, 133.5, 127.0, 123.7, 122.9, 120.1, 109.9, 101.8, 32.4, −0.4. MALDI MS m/z 435.59 (M^+, $C_{26}H_{25}N_5Si$ requires 435.60).

2,6-Bis(1′-methylbenzimidazoyl)-4-ethynylpyridine (3). 2,6-Bis(1′-methylbenzimidazoyl)-4-(trimethylsilylethynyl)pyridine (0.75 g, 1.7 mmol) was dissolved in a mixture of THF (25 mL), MeOH (25 mL), and NaOH (25 mL, 20%), and the reaction mixture was stirred for 4 h at room temperature. The organic layer was separated, and the aqueous layer was extracted with $CHCl_3$. The combined organic layers were washed with water, dried over anhydrous Na_2SO_4, reduced in vacuo, and purified by column chromatography (silica gel, $CHCl_3$) to yield **3** as an off-white solid (0.54 g, 1.5 mmol, 88%). ^1H NMR (300 MHz, $CDCl_3$): δ 8.48 (s, 2 H), 7.87−7.85 (m, 4 H), 7.46−7.34 (m, 4 H), 4.22 (s, 6 H), 3.41 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.9, 149.6, 142.7, 137.3, 132.9, 127.6, 123.9, 123.1, 120.4, 110.1, 83.4, 80.3, 32.6. MALDI MS m/z 363.48 (M^+, $C_{23}H_{17}N_5$ requires 363.41).

Synthesis of Macromonomer 4. 1,4-Dioctyloxy-2,5-diiodobenzene (**1**) (266.5 mg, 0.455 mmol), 1,4-diethynyl-2,5-bis(octyloxy)benzene (**2**) (157 mg, 0.410 mmol), 2,6-bis(1′-methylbenzimidazoyl)-4-ethynylenepyridine (**3**) (29.6 mg, 0.082 mmol), toluene (6.6 mL), and diisopropylamine (2.6 mL) were added to a two-neck round-bottom flask, and the solution was purged with nitrogen for 0.5 h. The reaction was degassed by a repeated sequence of freeze−pump−thaw cycles. $Pd(PPh_3)_4$ (47.4 mg, 0.04 mmol) and CuI (7.8 mg, 0.04 mmol) were added to the reaction under nitrogen, and the mixture was stirred at 70 °C overnight. Ammonium iodide salts formed immediately after the start of the reaction, and the mixture became highly fluorescent within 1 h. After 19 h, a small excess of **3** was added (16.5 mg, 0.04 mmol), and the reaction mixture was stirred for another 4 h. The suspension was subsequently poured hot into a saturated aqueous EDTA solution (70 mL), and the mixture was stirred for 1 h. The organic layer was separated, and the aqueous layer was extracted with $CHCl_3$. The combined organic layers were washed with deionized water, and the volume was reduced under vacuum. The concentrated organic layer was added dropwise to a rapidly stirred solution of MeOH. After stirring for 2 h, the orange precipitate was collected and washed with boiling MeOH, EtOH, CH_3CN, and room temperature hexanes and MeOH. The product was redissolved in a minimal amount of $CHCl_3$, reprecipitated into MeOH, washed as outlined above, and dried overnight in a vacuum at room temperature to yield **4** as an orange solid (290 mg, 86%): $X_n = 27$ by ^1H NMR. ^1H NMR (600 MHz, $CDCl_3$): δ 8.56 (s, 4 H, byproduct **5**, the integral is 8% relative to the corresponding signal of the end group at 8.54 ppm), δ 8.54 (s, 4 H, end groups), 7.89 (d, 4 H, $J_{H-H} = 7.8$ Hz, end groups + **5**), 7.48 (d, 4 H, $J_{H-H} = 7.8$ Hz, end groups + **5**), 7.42−7.36 (m, 8 H, end groups + **5**) 7.08 (s, 2 H, ar end group), 7.06 (s, 2 H, ar) 7.04 (s, 2 H, ar), 7.02 (s, 2 H, ar), 4.28 (s, 12 H, **5**, the integral is 8% relative to the corresponding signal of the end group at 4.27 ppm), 4.27 (s, 12 H, end groups), 4.08 (t, 4H, $J_{H-H} = 6.6$ Hz, OCH_2 end group) 4.03 (t, 4 H, $J_{H-H} = 6.6$ Hz, OCH_2), 1.86 (m, 4 H, CH_2), 1.52 (m, 4 H, CH_2), 1.37 (m, 4 H, CH_2), 1.27 (m, 12 H, CH_2), 0.87 (t, 6 H, $J_{H-H} = 6.6$ Hz, CH_3), 0.78. (t, 6 H, $J_{H-H} = 6.6$ Hz, CH_3 end group). ^{13}C NMR ($CDCl_3$, 600 MHz): δ 153.4, 149.8, 149.7, 142.6, 137.2, 128.2, 126.8, 123.7, 122.9, 120.3, 117.1, 114.2, 109.9, 91.6, 69.6, 32.5, 31.9, 29.4, 29.3, 29.2, 26, 22.7, 14.0. GPC (THF): PDI = 1.6; $M_n = 19\,700$; $M_w = 31\,500$.

Synthesis of 5. 2,6-Bis(1′-methylbenzimidazoyl)-4-ethynylenepyridine (**3**) (88 mg, 0.24 mmol), CuI (5 mg, 0.02 mmol), $Pd(PPh_3)_4$ (26 mg, 0.02 mmol), toluene (5 mL), and diisopropylamine (2 mL) were stirred under ambient atmosphere in a round-bottom flask at 72 °C for 24 h. The reaction was poured hot into a saturated aqueous solution of EDTA, and the mixture was stirred for 2 h. The organic layer was separated, washed with deionized water, and reduced under vacuum. The concentrated organic layer was added dropwise to a rapidly stirred solution of methanol upon which a brown precipitate was observed. The solid was collected by filtration and washed with boiling MeOH, EtOH, CH_3CN, and room temperature hexanes and MeOH. ^1H NMR (600 MHz, $CDCl_3$): δ 8.56 (s, 4 H), 7.88 (d, 4 H, $J_{H-H} = 6.9$ Hz), 7.48 (d, 4 H, $J_{H-H}, = 6.6$ Hz), 7.44−7.35 (m, 8 H), 4.27 (s, 12 H). ^{13}C NMR ($CDCl_3$, 600 MHz): δ 150.0, 149.3, 142.6, 137.2, 131.8, 127.5, 123.9, 123.1, 120.4, 109.9, 79.9, 78.3, 32.5. MALDI MS m/z 725.55 (M^+, $C_{46}H_{32}N_{10}$ requires 724.8).

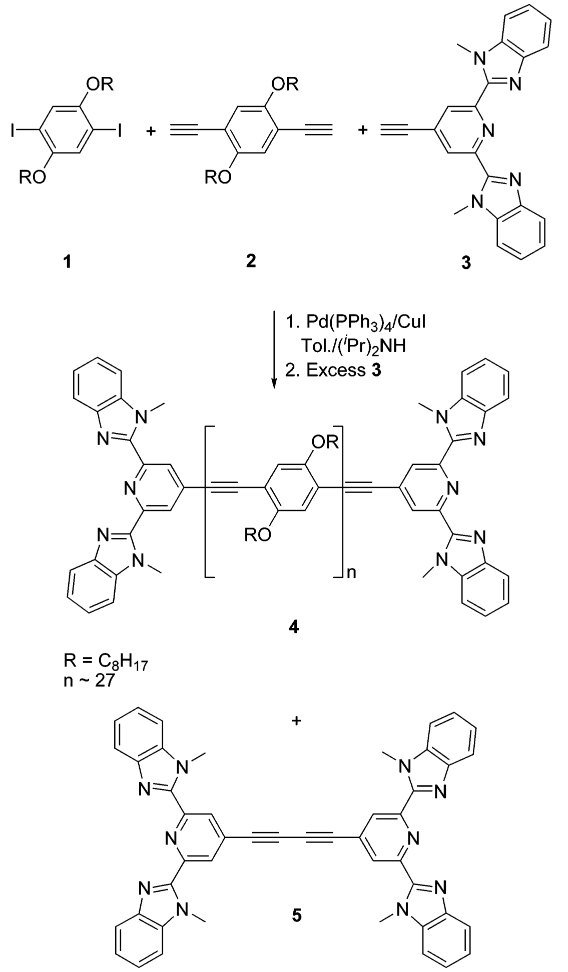
Typical Sample Preparation of Metallo-Supramolecular Polymers. To a stirred solution of macromonomer **4** (57.7 mg) in $CHCl_3$ (1.5 mL) was added a solution of $Zn(ClO_4)_2$ in CH_3CN (94 μL of a 0.068 M solution). Immediately upon addition, the mixture became highly viscous. The solvents were evaporated under vacuum, and a red film was obtained. This material was redissolved in $CHCl_3$ (3 mL), and a viscous red solution was obtained. Simple fiber samples were drawn from a portion of this mixture that was cast onto a glass substrate. Another portion of the solution was transferred to a cylindrical aluminum film caster (diameter 3 cm) with Teflon base. The solvent was slowly evaporated at room temperature over the course of 18 h. The resulting red film (diameter: 2.8 cm; thickness: 60 μm) was removed from the mold, dried under vacuum at room temperture for 20 h, and cut into smaller pieces for analysis by DMTA, TGA, UV−vis, and PL spectroscopy. Films of a thickness of less than 1.0 μm were prepared by spin-coating $CHCl_3$ solutions of the polymer (concentration ca. 1 mg/mL) onto glass slides.

PL Titration of 4 with $Zn(ClO_4)_2$. A solution of **4** (2.2×10^{-5} M) in a mixture of $CHCl_3/CH_3CN$ (9/1 v/v) was titrated with 15 μL aliquots of a solution of $Zn(ClO_4)_2$ (5.6×10^{-4} M) and **4** (2.2×10^{-5} M) in the same solvent mixture. The addition was done stepwise, and after each step, the formation of $[\mathbf{4}\cdot Zn(ClO_4)_2]_n$ was monitored by PL spectroscopy with excitation at 400 nm.

Results and Discussion

Synthesis of Macromonomer 4. The 2,6-bis(1′-methylbenzimidazolyl)pyridine (Mebip) end-capped poly(2,5-dioctyloxy-

Scheme 2. Synthesis and Molecular Structure of the Mebip End-Capped Poly(2,5-dialkoxy-*p*-phenylene ethynylene) Macromonomer 4 with Byproduct 5



p-phenylene ethynylene) macromonomer (**4**) was prepared in good yield (86%) via the Sonogashira−Heck cross-coupling reaction of aryl iodide (**1**) and aryl acetylene (**2**), using the Mebip derivative 2,6-bis(1′-methylbenzimidazolyl)-4-ethynylpyridine (**3**) as an end-capper (Scheme 2).

In view of the low solubility of high-molecular-weight PPEs with octyloxy side chains,[25] the number-average degree of polymerization, X_n, was limited to a target value of 20 by slightly offsetting the molar ratio of the two bifunctional monomers **1** and **2**. According to standard procedure,[25] the polycondensation reaction was performed using $Pd(PPh_3)_4/CuI$ as the catalyst system in a mixture of toluene and diisopropylamine. A small excess of the Mebip-end-capper **3** was added toward the end of the reaction with the objective to maximize end-capping of macromonomer **4**. A minor drawback to this protocol was encountered in the fact that the use of an excess of ethynylene **3** led to the formation of a minor amount of the Glaser-coupled diyne **5** as a byproduct (ca. 3−8% relative to **4**). The identity and concentration of this byproduct were ascertained by ^1H NMR experiments that were conducted with reference to an independently prepared sample of **5**. While **5**, at least under the experimental conditions employed here, could not be completely eliminated from the product, its presence, as will be discussed below, did not prevent the formation of mechanically stable films comprised of supramolecular polymers based on **4**.

The procedure for purification and isolation of macromonomer **4** varied significantly from that of normal PPEs. To ensure removal of any Mebip-binding residues of the Pd and Cu catalysts, the polymerization reaction mixture was stirred for an extended period over a saturated aqueous solution of EDTA and subsequently extensively extracted with a battery of solvents (see Experimental Section for details). Macromonomer **4**, which was completely soluble at concentrations of at least ≈40 mg/mL in solvents such as $CHCl_3$, toluene, and THF, was characterized by ^1H and ^{13}C NMR spectroscopy. As in earlier studies,[25] the number-average degree of polymerization, X_n, of ≈27, determined by ^1H NMR end-group analysis, was slightly higher than targeted (20). This is consistent with the loss of low-molecular-weight material during the reaction workup, which was evident from the color of the filtrates obtained upon precipitation of macromonomer **4**. The higher than expected value of X_n could also be related to incomplete end-capping of macromonomer **4** with Mebip groups (used for the end-group analysis), but no other end groups could be detected in the NMR spectra. A high degree of end-capping is also corroborated by GPC data, which reveal an M_n of ≈19 700 (which translates into an $X_n = 54$) and a polydispersity of 1.6. Since the GPC data were calibrated against polystyrene standards, the GPC X_n of **4** is considerably higher than the value obtained by NMR end-group analysis. The level of overestimation seen here for **4** is similar to that observed for an identical PPE that was end-capped with phenyl end groups,[26] suggesting that **4** is indeed end-capped with Mebip groups to a very high degree.

Optical Properties of Macromonomer 4. The photophysical characteristics of macromonomer **4** were investigated both in $CHCl_3$ solution and on spin-cast thin films; all spectroscopic data are summarized in Table 1, and absorption and emission spectra of **4** are shown in Figure 1. The solution absorption spectrum exhibits a main band centered at 448 nm and a weaker band around 319 nm. These transitions are associated with the the $\pi-\pi^*$ and $n-\pi^*$ transition of the polymer backbone, respectively. Optical excitation of **4** causes intense photoluminescence. The emission spectrum displays two well-resolved bands near 484 and 510 nm and exhibits features that are consistent with $\pi-\pi^*$ fluorescence. A comparison between the optical data of **4** and poly(2,5-dioctyloxy-*p*-phenylene ethynylene) without the Mebip end groups[25] reveals that these materials display virtually identical optical characteristics and that the Mebip end groups do not alter the electronic properties of the PPE backbone. Macromonomer **4** could readily be processed into homogeneous films of good optical quality by spin-coating from $CHCl_3$ solution. The absorption spectrum of a spin-cast film of macromonomer **4** shows a slight red shift when compared to solution (the transitions observed in solution at 448 and 319 nm now appear around 455 and 320 nm) and displays a new sharp feature at 485 nm (Figure 1b). The solid-state PL emission spectrum is also red-shifted and significantly broadened. These features are characteristic of PPE aggregation and pronounced intermolecular interactions.[25,27,28] It should be noted that the detailed features of the solid-state spectra are related to the degree of order, which is dependent on and can be controlled by the exact processing conditions and/or annealing above the glass transition temperature.

Supramolecular Polymerization of Macromonomer 4 with Zn^{2+} and Fe^{2+}. The formation of metallo-supramolecular polymers of the type $[4{\cdot}MX_2]_n$ is readily achieved by the addition of the metal ion salt dissolved in CH_3CN to a $CHCl_3$ solution of macromonomer **4** (Scheme 1). We have found that a variety of metals ions display appropriate interactions (i.e., large equilibrium constant and rapid complexation kinetics) that allow for supramolecular polymerization utilizing the terdentate

Table 1. Optical Absorption and PL Emission Data of Macromonomer 4 and Supramolecular Polymers Based on Equimolar Amounts of 4 and Zn^{2+} or Fe^{2+} Ions

	solution ($CHCl_3$)		thin film	
	absorption λ_{max} (nm)	emission $\lambda_{max}{}^{a}$ (nm)	absorption λ_{max} (nm)	emission $\lambda_{max}{}^{a}$ (nm)
4	319, 448	484, 510	320, 455, 485	543, 580
$[\mathbf{4}\cdot Zn(ClO_4)_2]_n$	n.a.[c]	480, 665[d]	321, 453, 485	670
$[\mathbf{4}\cdot Fe(ClO_4)_2]_n$	n.a.[c]	b	320, 444, 476, 635	–[b]

[a] Excitation at 400 nm. [b] Emission is fully quenched. [c] Not available due to the high extinction of concentrated solutions which display adequate binding. [d] Measured at a concentration of 1.86 mg of $[\mathbf{4}\cdot Zn(ClO_4)_2]_n$ in 1 mL of $CHCl_3$.

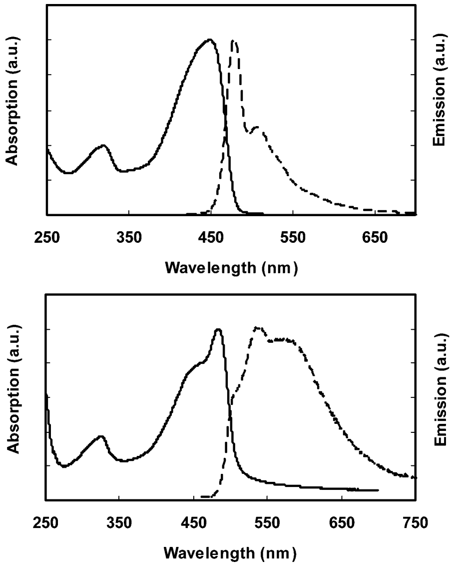


Figure 1. Optical absorption (solid lines) and PL emission (dashed lines) spectra of macromonomer **4** measured (top) in a $CHCl_3$ solution and (bottom) as a spin-cast thin film.

Mebip motif.[24] Here we employed Zn^{2+} and Fe^{2+}, with the intent to probe the influence of the different electronic characteristics of these metals on the resulting metallopolymers. Zn^{2+} features a fully occupied d-orbital ($3d^{10}$) and is a prototype for metals that show hardly any tendency for metal-to-ligand charge transfer (MLCT) with imine-type ligands.[29] In a variety of different systems, we previously observed orange photoluminescence from Zn—imine complexes,[21,30] and we speculated that this feature might be useful to tune the emission characteristics of the materials investigated here. By contrast, Fe^{2+} is well-known to form pronounced MLCT complexes and to act as a strong fluorescence quencher.[31] As expected, a 1:1 binding ratio of macromonomer **4** with both these metals lead to pronounced visual changes; the addition of Zn^{2+}, dissolved in CH_3CN, to a solution of **4** in $CHCl_3$ (38.5 mg/mL) resulted in an instantaneous and significant increase of the solution's viscosity. To ensure processability of the resulting metallopolymer by attenuating its molecular weight, a slightly higher than stoichiometric amount (1.04 equiv) of Zn^{2+} relative to the Mebip units present was employed. Evaporation of the solvent led to a red solid, which displayed appreciable mechanical properties. This metallopolymer could be redissolved in $CHCl_3$[32] and the resulting solutions were employed to produce (i) thin films for optical experiments by spin-coating (thickness < 1 μm), (ii) free-standing films (thickness ca. 60 μm) for mechanical experiments by solution-casting, and (iii) monofilaments by simple solution spinning. These samples, shown in Figure 2, visualize unequivocally that $[\mathbf{4}\cdot Zn(ClO)_4]_n$—very much in contrast to the neat macromonomer **4** and a poly(2,5-dioctyloxy-*p*-phenylene ethynylene) of similar X_n but without the Mebip end groups—offers considerable mechanical strength and flexibility. Metallopolymers based on **4** and Fe^{2+} were prepared in a fashion similar to those of Zn^{2+}. This led to the instantaneous formation of a green mixture and a significant increase of the solution's viscosity. Here, the solution was directly processed into thin films for optical experiments by spin-coating and free-standing films (thickness ca. 110 μm) for mechanical experiments by solution-casting.

Optical Properties of $[\mathbf{4}\cdot Zn(ClO_4)_2]_n$ and $[\mathbf{4}\cdot Fe(ClO_4)_2]_n$. The solid-state optical absorption spectrum of $[\mathbf{4}\cdot Zn(ClO_4)_2]_n$, measured on a thin film, prepared by spin-casting from a $CHCl_3$ solution, exhibits essentially the same features as a thin film of the neat macromonomer **4**, i.e., broad bands around 453 and 321 nm and a narrow aggregation band at 484 nm (Figure 3). The contribution of the aggregation band is more pronounced than in **4**, which appears to indicate a higher degree of long-range structural order for the metallopolymer (vide infra). Other than that, the similarity of the absorption spectra of **4** and $[\mathbf{4}\cdot Zn(ClO_4)_2]_n$ suggests that the band gap of the conjugated PPE sequences remains essentially unchanged upon binding of **4** with Zn^{2+}. With the goal of attaining further insight into the mechanism of the Zn^{2+}-mediated self-assembly process of **4**, $Zn(ClO_4)_2$ was titrated into a solution of **4**, and the resulting products were analyzed by means of PL spectroscopy. It should be noted that the precipitation of high-molecular-weight macromolecules at increased concentrations dictated that the PL titration experiment be performed at rather low concentrations (22 μM). As such, these conditions clearly favor the formation of oligiomeric species as opposed to high-molecular-weight aggregates. Figure 4a reveals that the emission associated with the PPE moieties is strongly quenched upon addition of Zn^{2+}. The inset of Figure 4a, which displays the relative emission intensity at λ_{max} (484 nm) as a function of Zn^{2+}, nicely shows that the effect depends on the concentration of Zn^{2+} in a nonlinear fashion and levels off at a Zn^{2+}:**4** ratio of 1. This observed leveling strongly suggests the formation of a metallo-supramolecular complex of the form $[\mathbf{4}\cdot Zn(ClO_4)_2]_n$. At this point the emission observed for the neat **4** is almost completely quenched; Figure 4a and its corresponding magnification at a Zn^{2+}:**4** ratio of 1.1:1, Figure 4b, also reveal some weak remaining emission that we impart to a small fraction of unbound macromonomer **4** (an artifact of the dilute conditions of the titration experiment) and the 1:1 Zn^{2+} complex of byproduct **5**, which is weakly luminescent and displays a broad maximum around 520 nm (see Supporting Information for spectra).

The addition of Fe^{2+} to macromonomer **4** causes, not unexpectedly, different optical changes than observed for Zn^{2+}. The absorption spectrum (Figure 5) exhibits essentially the same features as a thin film of the neat macromonomer **4**, i.e., broad bands around 445 and 320 nm and a narrow aggregation band at 476 nm. As expected, a characteristic metal-to-ligand charge-transfer absorption band centered at 635 nm can be observed, which is indicative of the formation of the 2:1 Mebip:Fe^{2+} complex, as it is required for the formation of the supramolecular polymer.[15,33] Furthermore, the addition of Fe^{2+} expectedly

Figure 2. A film (left) and fiber (middle) based on metallo-supramolecular polymer $[\mathbf{4}\cdot Zn(ClO_4)_2]_n$ and a film (right) comprised of metallo-supramolecular polymer $[\mathbf{4}\cdot Fe(ClO_4)_2]_n$.

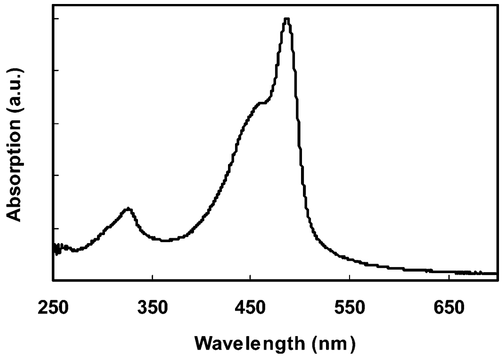


Figure 3. Optical absorption spectrum of a spin-cast film of the metallopolymer $[\mathbf{4}\cdot Zn(ClO_4)_2]_n$.

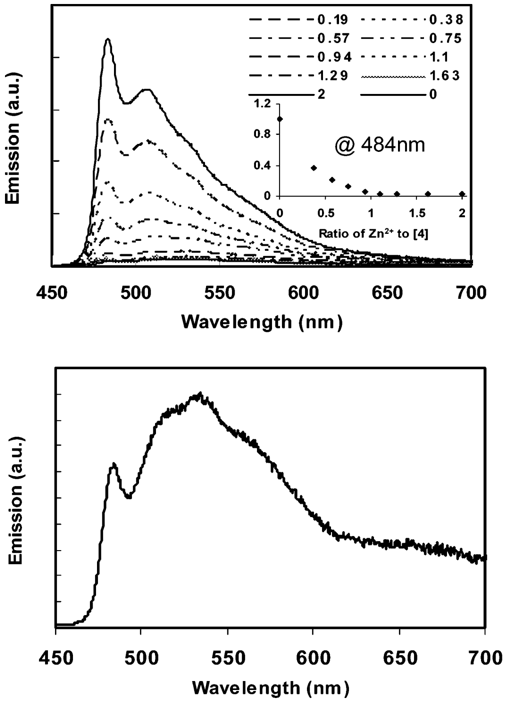


Figure 4. (a) PL emission spectra acquired under excitation at 400 nm upon titration of $Zn(ClO_4)_2$ into a solution of **4** (0.022 mM). Shown are spectra at selected Zn^{2+}:**4** ratios. The inset shows the emission intensity at 484 nm as a function of Zn^{2+}:**4** ratio. (b) PL emission spectra at a ratio of 1.1:1 Zn^{2+}:**4** (magnification ×30).

resulted in the complete quenching of the solid-state fluorescence.

Thermomechanical Properties of $[\mathbf{4}\cdot Zn(ClO_4)_2]_n$ and $[\mathbf{4}\cdot Fe(ClO_4)_2]_n$. The thermal and mechanical properties of the $[\mathbf{4}\cdot Zn(ClO_4)_2]_n$ and $[\mathbf{4}\cdot Fe(ClO_4)_2]_n$ supramolecular polymers and the parent macromonomer **4** were investigated by means of thermogravimetric analysis (TGA) and dynamic mechanical thermoanalysis (DMTA). TGA traces of neat **4** (Figure 6) acquired under a nitrogen atmosphere illustrate the onset of significant weight loss (2%) at 363 °C, corresponding to the thermal degradation of the polymer side chains. It should be noted though that thermal cross-linking of the ethynylene units, which cannot be discerned by TGA, typically occurs at temperatures above 150 °C. The Zn^{2+} and Fe^{2+} metallopolymers show a rather similar thermal behavior, but the 2% weight loss occurs at somewhat lower temperatures (313 and 250 °C, respectively), particularly in the case of Fe^{2+}. We ascribe this situation to the thermal degradation of the perchlorate counterions and are considering to investigate the influence of the counterion in more detail.

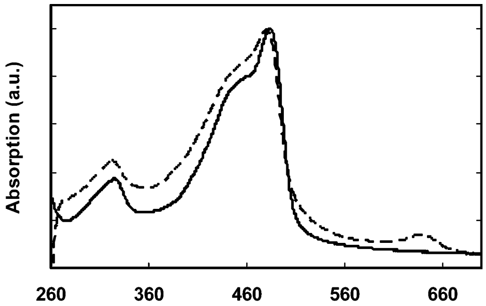


Figure 5. Optical absorption spectra of metallopolymer $[\mathbf{4}\cdot Fe(ClO_4)_2]_n$ measured on a spin-cast thin film (dashed) and macromonomer **4** (solid).

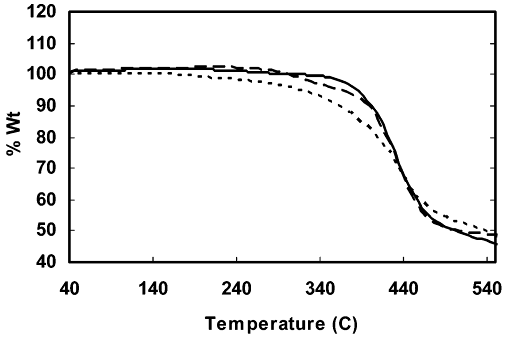


Figure 6. Thermogravimetric analysis (TGA) traces of **4** (solid), $[\mathbf{4}\cdot Zn(ClO_4)_2]_n$ (dashed), and $[\mathbf{4}\cdot Fe(ClO_4)_2]_n$ (dotted). Experiments were conducted under N_2 at a heating rate of 20 °C/min.

Gratifyingly, both $[\mathbf{4}\cdot Zn(ClO_4)_2]_n$ and $[\mathbf{4}\cdot Fe(ClO_4)_2]_n$ films displayed sufficient mechanical strength to allow for characterization by DMTA (Figure 7). Experiments were conducted in a temperature range of −20 to 100 °C. The moduli of $[\mathbf{4}\cdot Zn(ClO_4)_2]_n$ and $[\mathbf{4}\cdot Fe(ClO_4)_2]_n$ were determined to be ca. 160 and ca. 140 MPa at −20 °C and ca. 100 and ca. 83 MPa at 25 °C, respectively. A decrease in the modulus of both films was observed over the experimental temperature range; $[\mathbf{4}\cdot Fe(ClO_4)_2]_n$ exhibits a distinguishable transition at ~40 °C, which, in view of the striking similarity to the trace of a high-molecular-weight poly(2,5-dialkoxy-*p*-phenylene ethynylene) ($M_n \sim 83\,000$ g mol^{-1}) reported before,[34] we tentatively assign to a glass transition. While the moduli of $[\mathbf{4}\cdot Zn(ClO_4)_2]_n$ and $[\mathbf{4}\cdot Fe(ClO_4)_2]_n$ appear to be slightly lower than the latter material, they appear to be significant for any organometallic supramolecular conjugated polymer.

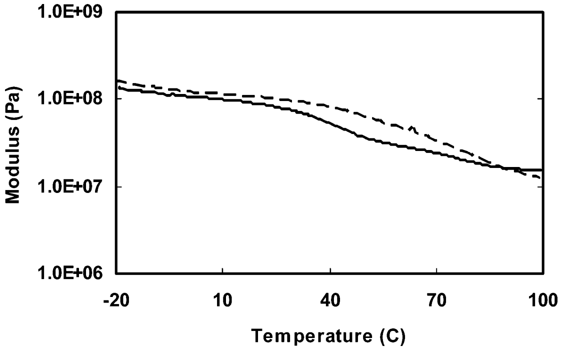


Figure 7. Dynamic mechanical thermoanalysis (DMTA) traces of [**4**·$Zn(ClO_4)_2$]$_n$ (dashed) and [**4**·$Fe(ClO_4)_2$]$_n$ (solid). Experiments were conducted under N_2 at a heating rate of 3 °C/min and a frequency of 1 Hz.

Conclusions

To overcome the inherent problems associated with processing functional high-molecular-weight conjugated polymers, we have utilized self-assembly polymerization. In this paper, we have shown that the supramolecular metallo-polymerization of PPE type MeBip end-capped macromolecules with both Zn^{2+} and Fe^{2+} ions can be employed to obtain mechanically stable materials. Thus, dynamic polymerization does offer an attractive approach to assemble high-molecular-weight conjugated macromolecules from well-defined, easy to process precursors.

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Supporting Information Available: PL and UV−vis spectra of compound **5** and the 1:1 $Zn(ClO_4)_2$:**5** complex; ^1H NMR spectra and GPC trace of macromonomer **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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