Poly(salphenyleneethynylene)s: soluble, conjugated metallopolymers that exhibit unique supramolecular crosslinking behavior†‡

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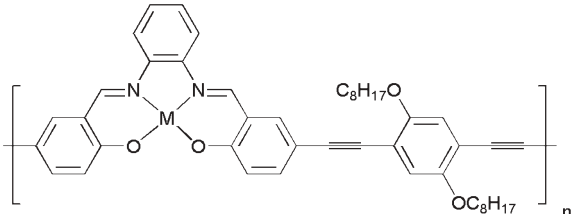
The synthesis of new soluble conjugated metallopolymers **4a–c** and **5a–c** containing Zn, Ni and Cu salphen derivatives is reported. The structures of the high molecular weight polymers are confirmed by NMR, IR, UV-vis, and fluorescence spectroscopic studies. Zinc-containing metallopolymer **4a** exhibits strong aggregation behavior in solution and in the solid state, and dissociation of the aggregates occurs upon addition of coordinating bases such as pyridine. A significant change to the luminescence of **4a** is observed, suggesting its potential application as a sensor for Lewis bases.

Introduction

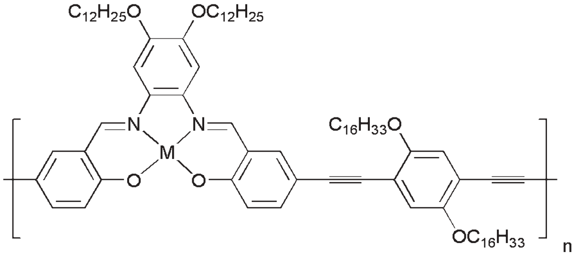
Recent developments in conjugated organic polymers, such as poly(*p*-phenylene)s (PPPs) and poly(*p*-phenylenevinylene)s (PPVs), have met with tremendous success and have led to useful applications such as organic light-emitting diodes,[1] semiconductors,[2] and photovoltaic devices.[3] Among the large variety of these conjugated polymers, poly(phenyleneethynylene)s (PPEs) are a relatively new and distinct class of conjugated polymers that have drawn a great deal of attention. Extensive research efforts have focused on the synthesis of new polymeric PPE materials,[4] along with other oligomeric structures such as macrocycles,[5] foldamers,[6] and dendrimers.[7] Potential applications for these materials are especially promising in the area of chemosensing and biosensing, where various PPE derivatives were demonstrated to function as sensors for chemical analytes such as trinitrotoluene (TNT) and biological agents such as DNA and carbohydrates.[8] Other potential applications as electroluminescent materials,[9] non-linear optical (NLO) materials,[10] and liquid crystals[11] were also explored.

In the search for novel PPEs with new and useful properties, researchers have synthesized and combined a diverse library of monomers, attaching functional units such as crown ethers[12] and carbohydrates[13] to the conjugated polymers. In particular, PPEs containing metal complexes such as porphyrins and ferrocenes have demonstrated unique electronic properties[14] and supramolecular behavior.[15] Although these organometallic PPEs exhibit attractive properties, relatively few examples of these metallopolymers have appeared in the literature, largely due to the synthetic difficulties in obtaining polymerizable metal-containing monomers and the polymers' insolubilities.[16]

In 2002, Lavastre and co-workers reported a large library of new luminescent conjugated polymers from a combinatorial synthesis and screening method.[17] Preliminary *in-situ* studies of the polymers indicated that the postulated structures **1** incorporating Zn^{2+} and Ni^{2+} salphen complexes possessed excellent luminescent characteristics, suggesting that they may be candidates for electroluminescent materials. We found that these polymers are insoluble, and we reported in a previous communication the synthesis of soluble high molecular weight derivatives, polymers **2**.[18] Studies of their luminescent properties indicated that these polymers were poorly emissive, and would not be suitable for electroluminescent devices.



1 (M = Zn, Ni)



2 (M = Zn, Ni, VO)

Although polymers **1** and **2** do not possess good luminescence, we anticipated these materials to have interesting properties in other areas due to the fact that Schiff base metal complexes, such as complexes of *N*,*N*′-bis(salicylidene)ethylenediamine, **3** ("M(salen)"), are known to exhibit interesting magnetic,[19] NLO,[20] oxygen transport,[21] catalytic,[22] and

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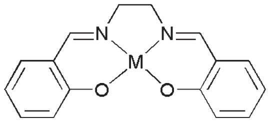
sensory[23] properties. In addition, our research group has investigated many macrocycles that contain salen complexes, and these may be thought of as cyclic oligomers of the polymers described in this paper. These macrocycles exhibit interesting supramolecular behavior, forming molecular cluster complexes and self-assembling into tubular assemblies.[24] Coordination and binding of small molecules to the macrocycles were found to strongly affect the optical properties of these materials, making them good candidates for sensors. Other researchers have reported the incorporation of salen-type complexes into conjugated backbones with variable success, and these have been utilized as catalysts, electroluminescent materials, and microspheres for photonic applications.[25] In this article, we report the synthesis of a new series of conjugated metallopolymers **4** and **5** designed to form linear and helical or zig-zag conformations, respectively. We report on their optical properties as well as the aggregation behavior of the zinc-containing polymers.



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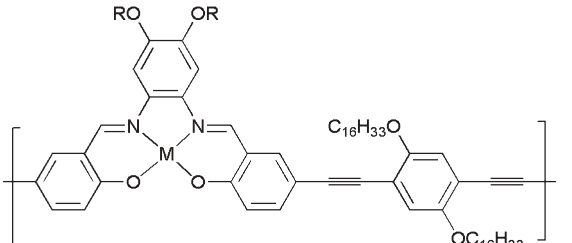
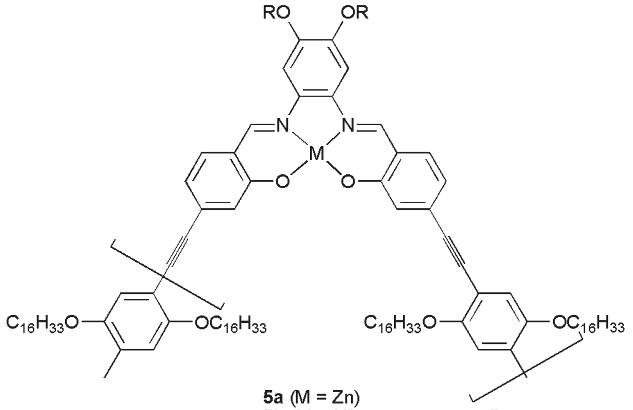


4a (M = Zn)
4b (M = Ni)
4c (M = Cu)
R = 2-butyloctyl



5a (M = Zn)
5b (M = Ni)
5c (M = Cu)
R = 2-butyloctyl

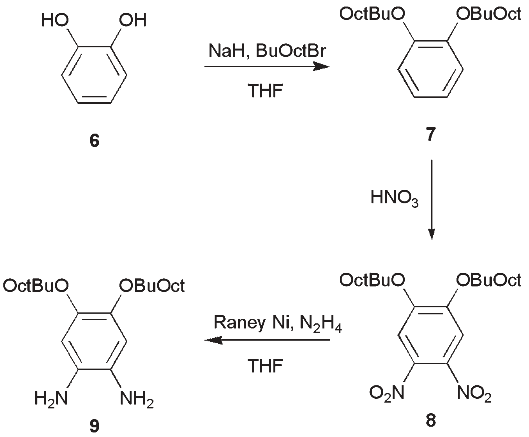
Results and discussion

Synthesis

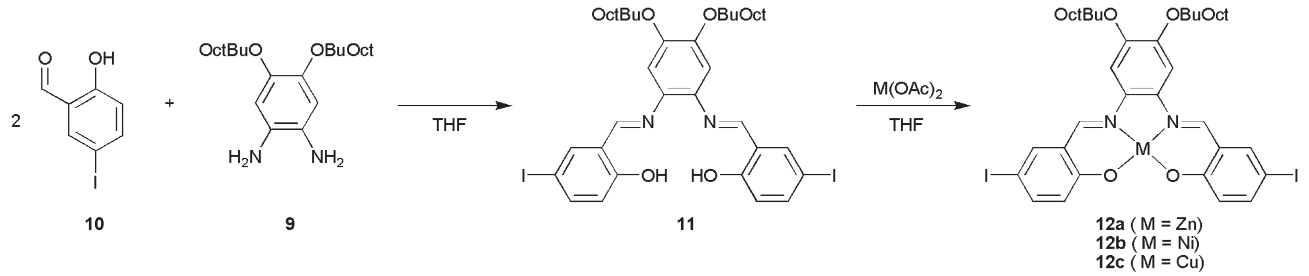
Previously we prepared soluble poly(salphenyleneethynylene)s (PSPEs) by incorporating two dodecyloxy substituents onto the salphen monomer. Although the resulting polymers were soluble in THF, long periods of stirring and heating were necessary to fully dissolve the polymers, and they become less soluble upon aging. Therefore, we sought to prepare PSPE derivatives with improved solubility through the addition of racemic 2-butyloctyloxy substituents, branched chains with chiral centers. Scheme 1 shows the synthetic route to the required precursor, substituted phenylenediamine **9**. Efforts to prepare compound **7** using standard Williamson ether synthesis conditions with K_2CO_3 or NaOH as the base led only to a low yield (24%) of **7**, with large amounts of mono-substituted side-product and unreacted catechol remaining even after 2 weeks of heating at reflux. The efficiency of this procedure can be significantly improved using NaH as the base, first forming salts of **6** followed by slow addition of 1-bromo-2-butyloctane; compound **7** was obtained as a colorless oil in excellent yield (96%). Compound **7** was subsequently nitrated with HNO_3 and reduced with Raney Ni and hydrazine to afford the target diamine **9**. Soluble salphen ligand **11** was prepared by reaction of 5-iodosalicylaldehyde **10** and diamine **9** under nitrogen in THF, and was isolated as a bright orange solid in 79% yield, Scheme 2. Reaction of **11** with $Zn(OAc)_2$, $Ni(OAc)_2$, and $Cu(OAc)_2$ afforded salphen monomers **12a–c** as yellow, red, and brown solids, respectively, in 85–92% yield. These monomers with iodo functionality opposite the hydroxyl groups are expected to give linear polymers.

In an effort to develop metallopolymers with the potential to form helices,[26] we constructed Schiff base monomers with a bent structure. Schiff base ligand **14** with iodo functionality *meta* to the hydroxyl moiety was prepared from 4-iodosalicylaldehyde **13** in 73% yield, Scheme 3. Subsequent reaction with $Zn(OAc)_2$, $Ni(OAc)_2$, and $Cu(OAc)_2$ yielded metal-containing monomers **15a–c**, respectively, in 90–93% yield.

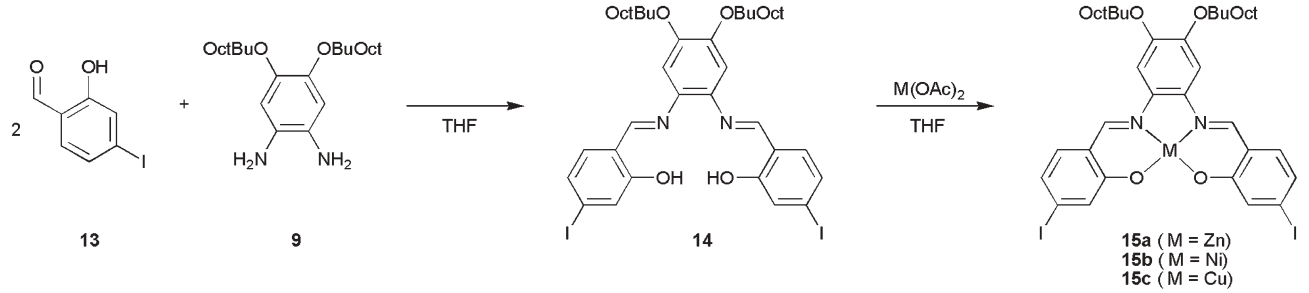
Compounds **12a–c** and **15a–c** were reprecipitated 2–3 times to afford pure compounds, and their compositions and purities were confirmed with ^1H and ^{13}C NMR spectroscopy, IR spectroscopy, UV-vis spectroscopy, MALDI-TOF mass spectrometry, and elemental analysis. The monomers all display an intense C=N stretching mode at 1600–1615 cm^{-1} in their IR spectra. Mass spectra of monomers **12a–c** and **15a–c** showed the expected molecular mass, and dimeric species were observed for both Zn monomers **12a** and **15a**. UV-vis spectra



Scheme 1 Synthesis of phenylenediamine **9**.



Scheme 2 Synthesis of monomers **12a–c**.



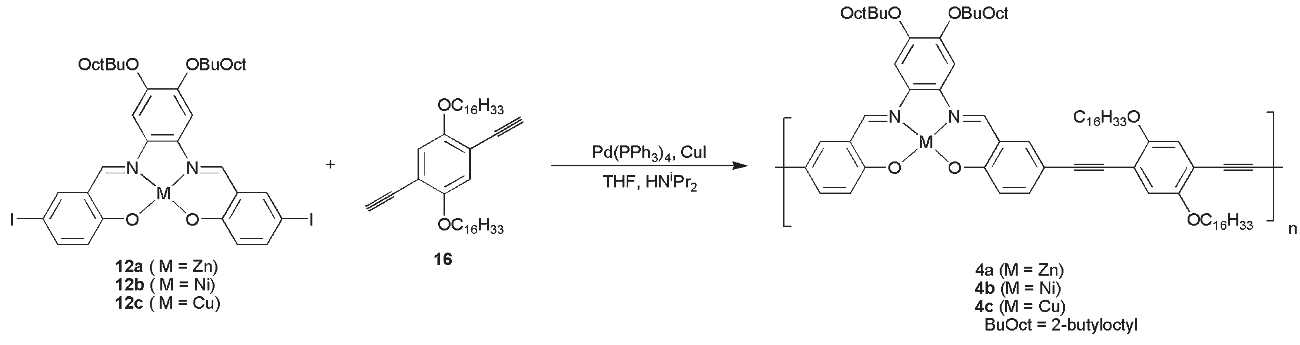
Scheme 3 Synthesis of monomers **15a–c**.

of the monomers all show multiple bands in the region between 200 and 550 nm, with strong absorption peaks centered at *ca.* 400 nm, and broad tails that extend to 550 nm. Fluorimetry measurements indicated that none of the monomers fluoresce, not surprising since they all have iodide substituents.

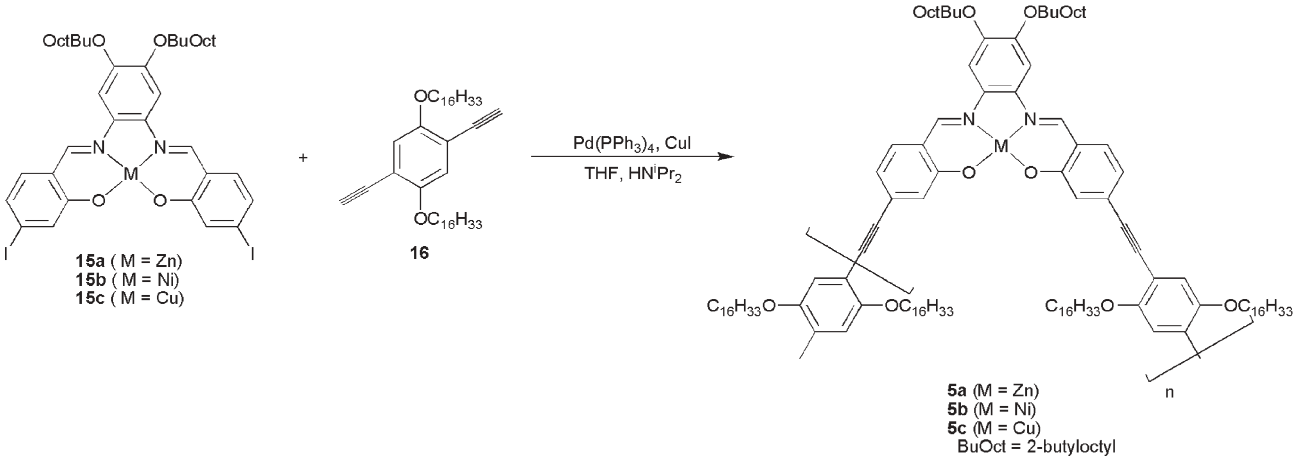
Polymerization of **12a–c** proceeds *via* Pd-catalyzed Sonogashira cross coupling in a mixture of THF–HN^{i}PR$_2$, affording high molecular weight polymers **4a–c** in 72–90% yield after 3–4 precipitations from THF into acetone and methanol, Scheme 4. Polymers **5a–c** were prepared employing an identical procedure, Scheme 5, but the resulting polymers were more soluble in organic solvents and were therefore purified by 3–4 precipitations from THF into methanol and hexane. Polymers **4a–c** readily dissolve in THF, but remain insoluble in other common organic solvents such as chloroform and toluene. These polymers form flexible free standing films, suggesting that their molecular weights are high enough to ensure substantial interchain entanglement, Fig. 1. Polymers **5a–c** are much more soluble, dissolving in solvents such as chloroform and THF. The improved solubility of **5** is likely a result of the polymers' helical or coil structures, inhibiting strong interchain interactions that can lead to aggregation. Consistent with this, polymers **5** do not readily form films, and they were isolated as waxy solids.

Polymer characterization

^{1}H NMR spectra of polymers **4a–b** and **5a–b** in CDCl$_3$ showed very broad peaks in the expected aromatic and alkyl regions, including a broad peak characteristic of the imine residue at *ca.* 8.5 ppm, Fig. 2.[27] The severe broadening is likely due to slow tumbling of the rigid polymers in the viscous solution, combined with strong aggregation between the polymer strands. The absence of terminal alkyne signals, residual monomer, or oligomer corroborated the formation of polymers with high molecular weight. IR spectroscopy confirms the absence of any starting monomers, and the presence of the $\nu_{C=N}$ (1600–1615 cm^{-1}) stretching mode verified that the salphen moiety remained intact. A new signal at *ca.* 2200 cm^{-1} was observed in all of the polymers, corresponding to the $C\equiv C$ stretching mode as expected with the formation of alkyne linkages in the polymeric backbone. UV-vis spectroscopy of the polymers showed peaks that are broader than for the



Scheme 4 Synthesis of conjugated metallopolymers **4a–c**.



Scheme 5 Synthesis of conjugated metallopolymers **5a–c**.

monomers, but the general absorption pattern resembled the starting salphen complexes. Absolute molecular weights of the polymers were established to be between *ca.* 19 000 and 74 000 Da (M_w) using GPC. The high molecular weights measured correspond to degrees of polymerization ranging from 14 to 55, and the molecular weights and other related information of the individual polymer samples are summarized in Table 1.

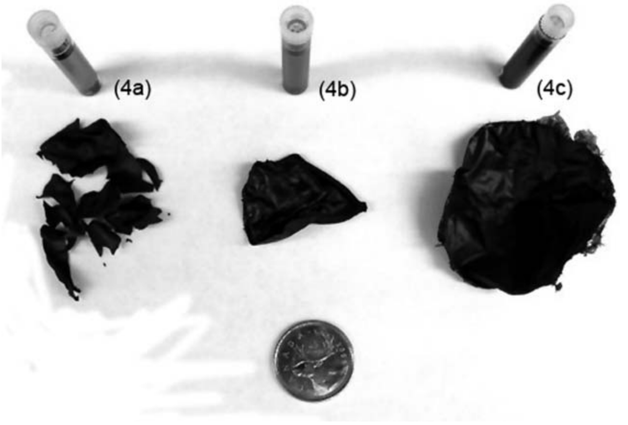


Fig. 1 Intensely colored films of polymers **4a–c** were obtained through simple suction filtration. The polymers dissolve in THF to give red solutions.

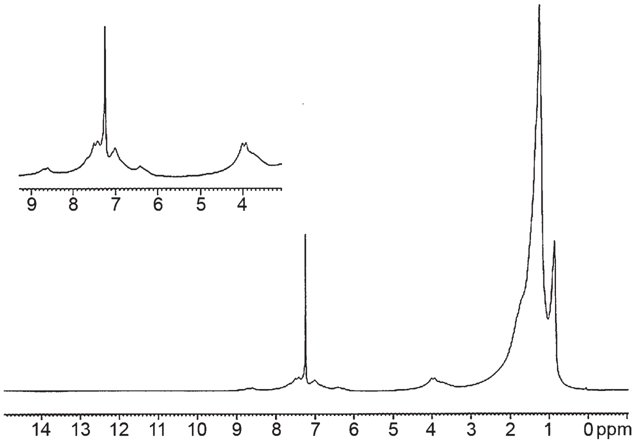


Fig. 2 ^{1}H NMR spectrum of polymer **4a** ($CDCl_3$ + 1% pyridine-d_5). Inset: Expanded view of region from 3 to 9 ppm.

Schiff base complexes have been incorporated into polymers to generate high temperature materials.[28] Thermal gravimetric analysis (TGA) indicated that PSPEs **4a–c** and **5a–c** are stable to *ca.* 200 °C, with less than 2% mass loss below this temperature. Differential scanning calorimetry (DSC) studies were performed on all of the polymers, but no noticeable transitions occurred between temperatures of −60 and 300 °C.

UV-vis spectra of polymers **4a–c** and **5a–c** show strong absorption peaks between *ca.* 400 and 500 nm, Fig. 3. Linear polymers **4a–c** all have similar absorption peaks centered at shorter wavelength (*ca.* 410 nm) and broad shoulders that extend toward 575 nm. On the other hand, absorption spectra of non-linear polymers **5a–c** possess broad peaks with less obvious shoulders. The linear polymers **4** all show significant blue-shifts in absorption relative to the non-linear analogues **5**. We postulate that there is extended conjugation through the aromatic system on the salphen unit in the case of non-linear polymers **5**, whereas in linear polymers **4** the conjugation pathway is interrupted by the metal centers, leading to shorter conjugation length and thus a blue-shifted absorption. To support our observations, the absorption spectra of model compounds **17** and **18** with phenylacetylene substituents *para* and *meta* to the phenol moiety, respectively, were compared. As shown in Fig. 4, the absorption spectrum of **18** is slightly red-shifted in comparison to that of **17**, but the absorption shoulder extends to significantly longer wavelength (*ca.* 20 nm shift). This observed change in absorption behavior between

Table 1 Molecular weights (M_w, M_n) and polydispersities of polymers **4a–c** and **5a–c**. Measurements were made with a GPC system equipped with triple detection (refractive index, light-scattering, and viscosity)

	4a	4b	4c	5a	5b	5c
M_w	18700	73600	33700	32800	60400	63200
M_n	17200	52000	32400	24300	42400	50700
PDI	1.09	1.42	1.04	1.35	1.43	1.25

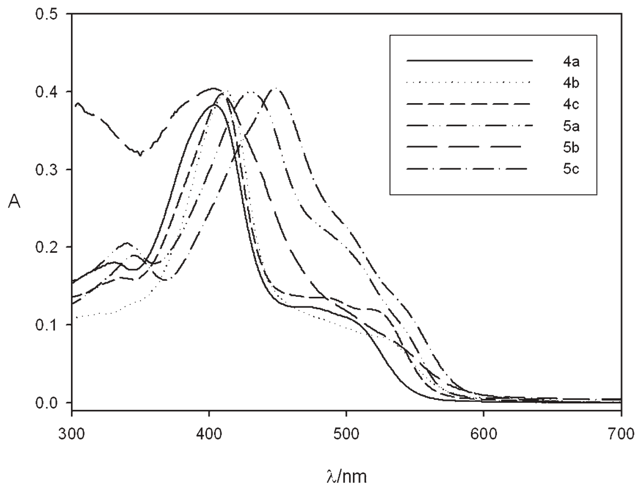
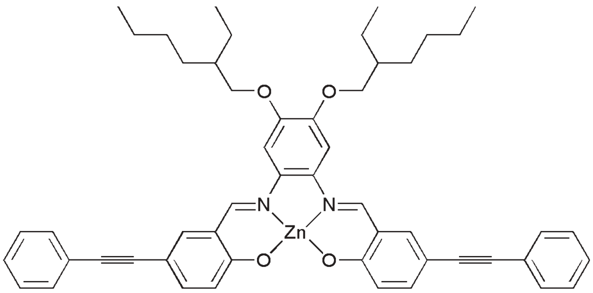


Fig. 3 UV-vis absorption (normalized) spectra of polymers **4a–c** and **5a–c** in CH_2Cl_2.

the model compounds agrees with the observed trend for the polymers, correlating the absorption changes with increase of conjugation.



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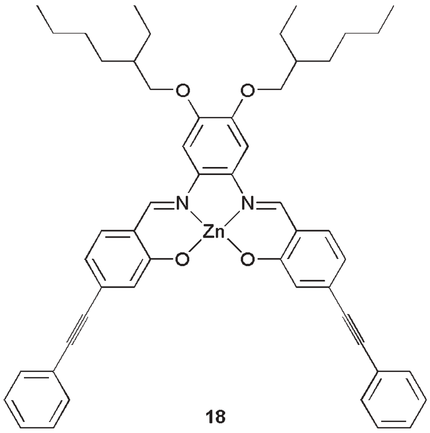

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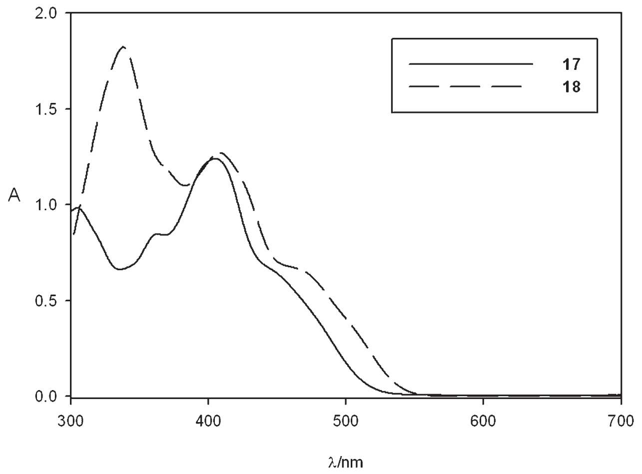

Fig. 4 UV-vis absorption (normalized) spectra of **17** and **18** in CH_2Cl_2.

Aggregation

Self-association of Zn salen complexes is well documented in the literature, forming dimeric complexes in solution and the solid state. In rigid salphen ligands, the Zn^{2+} ion is unable to acquire a tetrahedral geometry, and therefore dimerizes to expand its coordination number as shown in Fig. 5.[29] We have reported the reversible aggregation of zinc-containing Schiff base macrocycles mediated by a Zn···O interaction between the phenolic oxygen and Zn^{2+} metal center of Zn salphen moieties.[24,30] In these phenyleneethynylene-type macrocycles, strong aggregation was observed in non-polar solvents, but deaggregation occurred upon the addition of coordinating ligands such as pyridine that competitively coordinate to the zinc ions.

Zinc-containing Schiff base polymer **4a** is insoluble in most organic solvents, such as CH_2Cl_2. Upon addition of *ca.* 1% pyridine to a sample of **4a** in CH_2Cl_2, the polymer dissolved. On the other hand, when 2,6-lutidine was added instead of pyridine, the polymer was not dissolved, even in pure lutidine. Lutidine is a stronger base than pyridine, but bulky methyl substituents inhibit coordination to metal centers. This observation suggested that the coordination of pyridine to the polymer was necessary to disrupt strong intermolecular interactions between the polymer strands.

To further probe this interaction, we studied the addition of Lewis bases to the polymer in solution. The UV-vis spectrum of polymer **4a** in CH_2Cl_2 shows an absorption peak at 400 nm with a broad shoulder that extends to approximately 550 nm. Fluorescence measurements in CH_2Cl_2 indicated that the polymer is weakly luminescent, having a quantum yield of only 0.073%. Upon the addition of pyridine to a solution of **4a** in CH_2Cl_2, a gradual but minor decrease in the absorption maximum at *ca.* 400 nm was observed, together with small increases to the absorption shoulder at *ca.* 500 nm, Fig. 6a. A pseudo-isosbestic point was observed at *ca.* 530 nm, but was

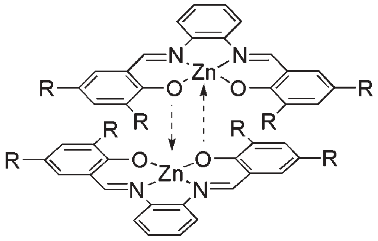

Fig. 5 Illustration of dimerization in Zn salphen complexes. Strong interactions between the Zn^{2+} center and the phenolic oxygens of the metal complexes hold the dimer together.

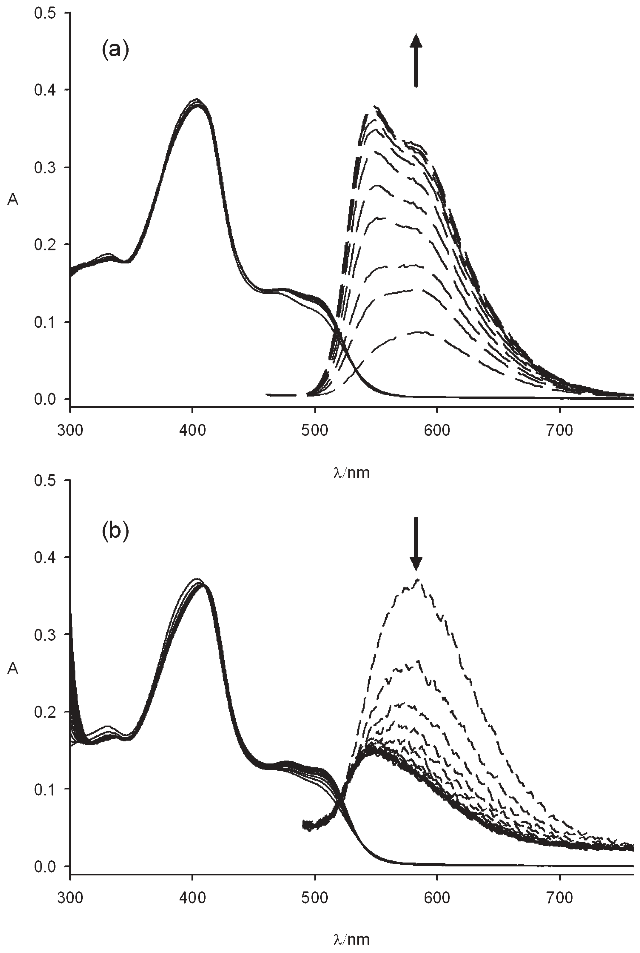

Fig. 6 UV-vis and fluorescence spectra of **4a** (CH_2Cl_2, 5.00×10^{-6} M) titrated with a) pyridine (1.03×10^{-6} to 1.03×10^{-5} M; step size: 1.03×10^{-6} M) and b) 4,4′-bipyridine (4.30×10^{-5} to 6.45×10^{-4} M; step size: 4.30×10^{-5} M).

not well defined, consistent with the complexity of the polymer deaggregation process as pyridine binds to the metal salphen complexes. In the emission spectra, a much more pronounced effect was observed upon the addition of pyridine, where the fluorescence maximum at *ca*. 580 nm increased about four-fold after 2 equivalents of pyridine were added (Φ = 0.27% after saturation). A blue shift from 590 to 546 nm was also observed in the fluorescence spectrum. When 2,6-lutidine was added to solutions of polymer **4a** in solution, no changes in the absorption or emission spectra were observed.

For comparison, we examined model compound **18**, a Zn salphen complex that is monomeric in solution. As shown in Fig. 7, the absorption spectrum of **18** changes gradually with the addition of pyridine or 4,4′-bipyridine, but no significant changes to the fluorescence spectra are observed.

These results suggest that in solution polymer **4a** exists in an aggregated (crosslinked) state held together by Zn···O interactions. In this form, the luminescence is mostly quenched due to excimer-like inter-strand interactions, along with energy transfer of the polymer absorption into localized states of the metal complexes. Upon addition of a Lewis base that can coordinate to the Zn^{2+} ions, the crosslinks are broken and the polymer becomes more soluble. The polymer emission also increases in intensity and undergoes a blue shift, supporting the disruption of an excimer-like species.

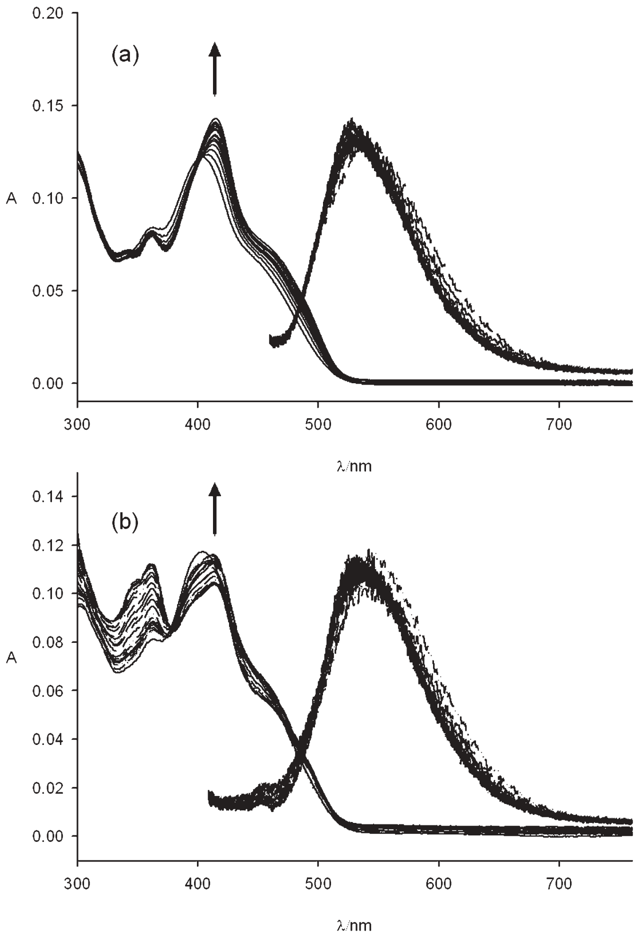

Fig. 7 UV-vis and fluorescence spectra of **18** (CH_2Cl_2, 5.00×10^{-6} M) titrated with a) pyridine (1.03×10^{-8} to 1.65×10^{-7} M; step size: 1.03×10^{-8} M) and b) 4,4′-bipyridine (1.08×10^{-6} to 2.40×10^{-5} M; step size: 1.08×10^{-6} M).

We investigated the addition of 4,4′-bipyridine to polymer **4a** to see whether a ladder polymer would form, where the metal ions are bridged by the bipyridine ligand. A similar approach to porphyrin-based PPE ladder polymers has been reported by Anderson and co-worker.[31] Addition of bipyridine to **4a** in CH_2Cl_2 yielded similar changes to the absorption spectrum as for the addition of pyridine, but an abrupt decrease of the emission peak was observed, Fig. 6b. The decrease in emission ceased after *ca.* 0.2 equivalents of 4,4′-bipyridine were added to the sample, and the Stern–Volmer plot for the fluorescence quenching shows a non-linear curve, indicative of static quenching. The observed behavior is consistent with the formation of polymers with the bidentate 4,4′-bipyridine ligand bridging the polymer strands.

Polymer **5a** is expected to adopt a helical or coil structure in which inter-strand interactions are reduced in comparison to **4a**, inhibiting aggregation. Polymer **5a** is considerably more soluble than **4a**, suggesting that there are fewer crosslinks within the polymer. Moreover, the optical properties of polymer **5a** are affected by Lewis bases in a different way

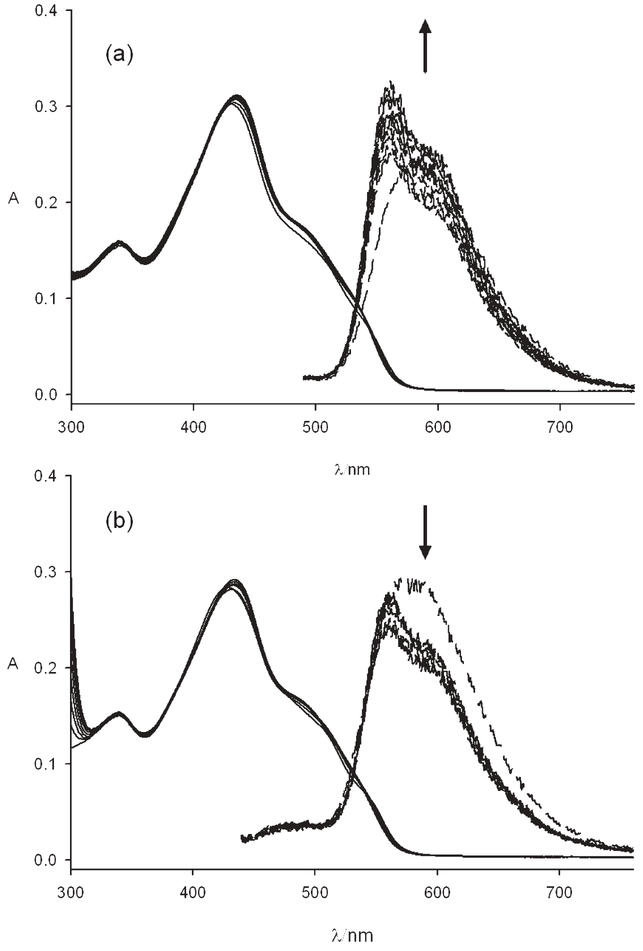

Fig. 8 UV-vis and fluorescence spectra of **5a** (CH_2Cl_2, 5.00 × 10^{-6} M) titrated with a) pyridine (1.03 × 10^{-6} to 1.03 × 10^{-5} M; step size: 1.03 × 10^{-6} M) and b) 4,4′-bipyridine (4.30 × 10^{-5} to 3.01 × 10^{-4} M; step size: 4.30 × 10^{-5} M).

than polymer **4a**. As shown in Fig. 8, gradual changes were observed in the absorption spectra upon addition of pyridine or 4,4′-bipyridine, suggesting that coordination of the ligands occurs as in the case of polymer **4a**. However, only a very minor increase to the polymer's emission at 590 nm was observed upon addition of pyridine, and a similarly small decrease to the fluorescence peak occurred in response to the addition of 4,4′-bipyridine. These results from UV-vis and fluorescence spectroscopy, along with sharper signals in the ^{1}H NMR spectrum and the good solubility of this material, confirm that the polymer **5a** has a weaker tendency to form strong aggregates in the dilute CH_2Cl_2 solution. However, it is likely that intramolecular association of the salphen moieties leads to the weak luminescence (Φ = 0.15%).

Polymers **4b–c** and **5b–c** containing square planar Ni^{2+} and Cu^{2+} ions showed no significant changes to their absorption spectra upon the addition of coordinating bases. The lack of response from these polymers is expected as the metal centers are square planar in geometry and do not readily expand their coordination numbers.

Overall, we believe that the Zn···O interaction is involved in crosslinking conjugated polymer **4a**. This supramolecular interaction can be disrupted by addition of bases or by designing a polymer structure that reduces interchain interactions, as in polymer **5a**. This new reversible crosslinking mechanism involving Zn···O interactions, illustrated in Fig. 9, is potentially useful for developing thermoplastic and elastomeric materials.

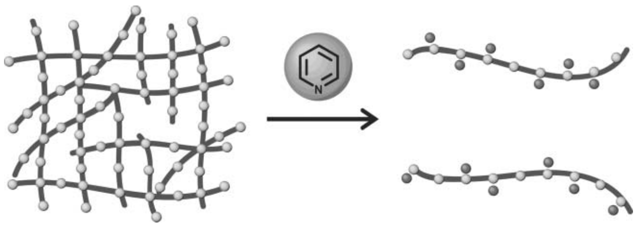

Fig. 9 Cartoon illustrating the disruption of the polymer crosslinks upon the addition of pyridine.

Conclusions

In summary, we have prepared a new series of high molecular weight conjugated PPE polymers containing Zn, Ni, and Cu salphen metal complexes in the backbone. The insolubility of the rigid metallopolymers was overcome through the addition of racemic branched alkoxy substituents, and the introduction of a bent geometry to the conjugated backbone. We have observed strong aggregation of the linear Zn metallopolymers that is facilitated by the presence of Zn···O interactions. Deaggregation occurs when the polymer is treated with a coordinating base such as pyridine, and a strong response in polymer emission makes these polymers possible sensors for Lewis bases. Future work will probe the effects of different Lewis bases on the optical properties of polymer **4a**, with the goal of making a conjugated polymer with optical properties that can be tuned by addition of ligands.

Experimental

Materials

Copper(I) iodide, zinc(II) acetate, nickel(II) acetate, and copper(II) acetate were obtained from Aldrich. Tetrakis-(triphenylphosphine)palladium was obtained from Strem Chemicals, Inc. Deuterated solvents were obtained from Cambridge Isotope Laboratories, Inc. Tetrahydrofuran was distilled from sodium/benzophenone under N_2. NH^iPr_2 was distilled from NaOH under N_2. 5-Iodosalicylaldehyde **10**, 4-iodosalicylaldehyde **13**, and 1,4-dihexadecyloxy-2,5-diethynylbenzene **16** were prepared by literature methods.[32] The synthesis of model compound **18** was previously reported by our group,[30] and compound **17** was prepared by an analogous procedure.

UV-vis and fluorescence measurements

Polymers **4a–c** and **5a–c** were initially dissolved in a small amount of THF (*ca.* 2 mL) and diluted to appropriate concentrations (1.0 × 10^{-6} M for quantum efficiency measurements, 5.0 × 10^{-6} M for titration studies) with CH_2Cl_2 so that the final concentration of THF was <0.1%. Titration experiments were performed in a 1 cm cuvette. The addition of appropriate Lewis bases in CH_2Cl_2 to the polymer samples with a microsyringe was followed by a short period of mixing and subsequent UV-vis and fluorescence measurements. No significant differences in the absorption and emission spectra were found between samples of polymers **5a** prepared *via* the above method and samples prepared by dilution in pure CH_2Cl_2.

Syntheses

Synthesis of Schiff base ligand (11). A solution of **9** (0.500 g, 1.05 mmol) and **10** (0.572 g, 2.31 mmol) in 20 mL of THF was heated to reflux for 24 h. After cooling to room temperature, 50 mL of MeOH was added to the reaction mixture under air to precipitate the orange product. Precipitation in THF–MeOH was repeated once to afford **11** (0.735 g, 0.785 mmol, 79%) as an orange solid (Found: C, 56.41; H, 6.64; N, 3.24. Calc. for $C_{44}H_{62}I_2N_2O_4$ requires C, 56.41; H, 6.67; N, 2.99%); λ_{max} (CH_2Cl_2)/nm 361 (log ε 1.67), 390 (1.60); ν_{max}(KBr)/cm^{-1} 2956, 2926, 2856, 1889, 1612, 1557, 1510, 1471, 1351, 1272, 1220, 1410, 1351, 1272, 1220, 1180, 1130, 1018, 933, 870, 845, 819, 766, 727; δ_H (400 MHz, $CDCl_3$) 13.19 (s, 2H, O*H*), 8.53, (d, *J* = 6.8 Hz, 2H, C*H*=N), 7.65 (d, *J* = 2 Hz, 2H, aromatic C*H*), 7.55 (q, *J* = 2, 10.8 Hz, 2H, aromatic C*H*), 6.81 (d, *J* = 8.8 Hz, 2H, aromatic C*H*), 6.74 (s, 2H, aromatic C*H*), 3.91 (d, *J* = 5.6 Hz, 4H, OCH_2), 1.83 (m, 2H, CH_2), 1.25–1.60 (m, 32H, CH_2), 0.87 (m, 12H, CH_2); δ_C (100.6 MHz, $CDCl_3$) 161.0, 160.2, 150.0, 141.4, 140.3, 135.0, 121.8, 120.1, 104.2, 79.8, 72.5, 38.4, 32.1, 31.6, 31.4, 30.0, 29.3, 27.1, 23.3, 22.9, 14.3; *m*/*z* (MALDI-TOF) 937.3 (M + H$^+$, Calc. 937.3); mp 166–168 °C.

Synthesis of zinc monomer (12a). Compound **11** (0.300 g, 0.320 mmol) and zinc acetate dihydrate (0.084 g, 0.038 mmol) were combined in 10 mL of THF under air. The reaction was heated to reflux for 24 h to give a yellow solution. Cooling to room temperature followed by addition of 40 mL of MeOH furnished **12a** (0.289 g, 0.289 mmol, 90%) as a yellow solid (Found: C, 55.24; H, 6.53; N, 3.19. Calc. for $C_{44}H_{60}I_2N_2O_4Zn$ requires 52.84; H, 6.05, N, 2.80%); λ_{max} (CH_2Cl_2)/nm 304 (log ε 1.96), 402 (2.34); ν_{max}(KBr)/cm^{-1} 2918, 2859, 1888, 1614, 1504, 1466, 1374, 1309, 1263, 1218, 1170, 1139, 1119, 1018, 961, 937, 873, 826, 773, 726; δ_H (400 MHz, DMSO-d$_6$) 8.94, (d, *J* = 6.8 Hz, 2H, C*H*=N), 7.77 (d, *J* = 2 Hz, 2H, aromatic C*H*), 7.45 (s, 2H, aromatic C*H*), 7.38 (q, *J* = 2.4, 11.2 Hz, 2H, aromatic C*H*), 6.54 (d, *J* = 8.8 Hz, 2H, aromatic C*H*), 3.98 (d, *J* = 4.8 Hz, 4H, OCH_2), 1.76 (b, 2H, CH_2), 1.2–1.5 (m, 32H, CH_2), 0.87 (m, 12H, CH_3); δ_C (100.6 MHz, DMSO-d$_6$) 170.8, 159.5, 149.3, 143.1, 141.1, 132.5, 125.8, 122.6, 100.3, 71.9, 71.0, 37.6, 31.3, 31.0, 30.6, 29.2, 28.6, 26.3, 22.5, 22.1, 13.9; *m*/*z* (MALDI-TOF) 998.3 (M$^+$, Calc. 998.2), 2000.5 (dimer M$_2^+$, calc. 1996.4); mp decomp. >290 °C.

Synthesis of nickel monomer (12b). Monomer **12b** was prepared by a procedure identical to that for **12a** except nickel acetate was used in the place of zinc acetate. The monomer was isolated as a red solid (85%) (Found: C, 53.11; H, 6.44; N, 2.96. Calc. for $C_{44}H_{60}I_2N_2O_4Ni$ requires 53.19, H, 6.09; N, 2.82%); λ_{max} (CH_2Cl_2)/nm 267 (log ε 7.11), 387 (3.80), 493 (1.42); ν_{max}(KBr)/cm^{-1} 2928, 2854, 1607, 1590, 1556, 1515, 1452, 1411, 1368, 1318, 1279, 1245, 1224, 1184, 1140, 1115, 1017, 933, 821, 787; δ_H (400 MHz, $CDCl_3$) 7.77, (s, 2H, C*H*=N), 7.52 (s, 2H, aromatic C*H*), 7.32 (d, *J* = 9.2 Hz, 2H, aromatic C*H*), 6.90 (s, 2H, aromatic C*H*), 6.73 (d, *J* = 8.8 Hz, 2H, aromatic C*H*), 3.94 (d, *J* = 5.2 Hz, 4H, OCH_2), 1.83 (m, 2H, CH_2), 1.33 (m, 32H, CH_2), 0.89 (m, 12H, CH_3); δ_C (100.6 MHz, $CDCl_3$) 164.7, 151.2, 150.5, 142.5, 140.8, 135.8, 124.2, 123.0, 98.0, 75.6, 72.4, 38.3, 32.2, 31.5, 31.2, 30.0, 29.4, 27.2, 23.3, 23.0, 14.4; *m*/*z* (MALDI-TOF) 992.3 (M$^+$, Calc. 992.2); mp decomp. >260 °C.

Synthesis of copper monomer (12c). Monomer **12c** was prepared by a procedure identical to that for **12a** except copper acetate was used in the place of zinc acetate. The monomer was isolated as a brown solid (92%) (Found: C, 53.33, H, 6.12, N, 3.18. Calc. for $C_{44}H_{60}I_2N_2O_4Cu$ requires C, 52.94; H, 6.06; N, 2.81%); λ_{max} (CH_2Cl_2)/nm 255 (log ε 6.08), 373 (2.50), 420 (3.40); ν_{max}(KBr)/cm^{-1} 2924, 2855, 1894, 1732, 1607, 1589, 1507, 1457, 1371, 1316, 1246, 1220, 1175, 1138, 1118, 1017, 956, 824, 776, 726; *m*/*z* (MALDI-TOF) 997.8 (M$^+$, Calc. 998.3); mp 230–232 °C.

Synthesis of Schiff base ligand (14). A solution of **9** (0.617 g, 1.29 mmol) and **13** (0.706 g, 2.85 mmol) in 20 mL of THF was heated to reflux for 24 h. After cooling to room temperature, 50 mL of MeOH was added to the reaction mixture under air to precipitate the orange product. Precipitation in THF–MeOH was repeated once to afford **14** (0.883 g, 0.942 mmol, 73%) as an orange solid (Found: C, 56.58; H, 6.67; N, 3.16. Calc. for $C_{44}H_{62}I_2N_2O_4$ requires C, 56.41; H, 6.67; N, 2.99%); λ_{max} (CH_2Cl_2)/nm 289 (log ε 3.12), 344 (2.19), 387 (1.93); ν_{max}(KBr)/cm^{-1} 2927, 2857, 1601, 1553, 1515, 1484, 1464, 1358, 1268, 1252, 1018, 1060, 1018, 939, 905, 860, 850, 793; δ_H (400 MHz, $CDCl_3$) 13.38 (s, 2H, O*H*), 8.51, (s, 2H, C*H*=N), 7.42 (s, 2H, aromatic C*H*), 7.24 (q, *J* = 0.8, 8.8 Hz, 2H, aromatic C*H*), 7.03 (d, *J* = 8.0 Hz, 2H, aromatic C*H*), 6.75 (s, 2H, aromatic C*H*), 3.91 (d, *J* = 5.2 Hz, 4H, OCH_2), 1.83 (m, 2H, CH_2), 1.2–1.6 (m, 32H, CH_2), 0.87 (m, 12H, CH_3); δ_C (100.6 MHz, $CDCl_3$) 161.5, 161.3, 149.9, 135.0, 133.0, 128.5, 127.1, 119.0, 104.7, 99.9, 72.6, 38.4, 32.1, 31.6, 31.3, 30.0, 29.4, 27.1, 23.3, 22.9, 14.1; *m*/*z* (MALDI-TOF) 937.3 (M + H$^+$, Calc. 937.3); mp 99–101 °C.

Synthesis of zinc monomer (15a). Compound **14** (0.300 g, 0.320 mmol) and zinc acetate dehydrate (0.084 g, 0.038 mmol) were combined in 10 mL of THF under air. The reaction was heated to reflux for 24 h to give a yellow solution. Cooling to room temperature followed by addition of 40 mL of MeOH furnished **15a** (0.294 g, 0.294 mmol, 92%) as a yellow solid (Found: C, 52.48; H, 6.20; N, 3.20. Calc. for $C_{44}H_{60}I_2N_2O_4Zn$ requires C, 52.84; H, 6.05; N, 2.80%); λ_{max} (CH_2Cl_2)/nm 312 (log ε 3.04), 390 (3.28); ν_{max}(KBr)/cm^{-1} 2925, 2856, 1610, 1579, 1502, 1463, 1405, 1376, 1268, 1217, 1174, 1117, 911, 865, 833, 774, 732; δ_H (300 MHz, DMSO-d$_6$) 8.92, (s, 2H, C*H*=N), 7.43 (s, 2H, aromatic C*H*), 7.17 (d, *J* = 9 Hz, 2H, aromatic C*H*), 7.11 (s, 2H, aromatic C*H*), 6.85 (q, *J* = 3.0, 9.0 Hz, 2H, aromatic C*H*), 3.98 (d, *J* = 3.0 Hz, 4H, OCH_2), 1.75 (b, 2H, CH_2), 1.2–1.5 (m, 32H, CH_2), 0.86 (m, 12H, CH_3); δ_C (100.6 MHz, DMSO-d$_6$) 171.2, 160.3, 149.2, 137.0, 132.5, 131.6, 121.8, 119.3, 111.1, 102.5, 100.5, 71.1, 31.3, 31.0, 30.6, 29.2, 28.6, 26.3, 22.5, 22.1, 13.9; *m*/*z* (MALDI-TOF) 998.3 (M^+, Calc. 998.2), 1997.4 (dimer $(M_2 + H)^+$, Calc. 1996.4); mp decomp. >320 °C.

Synthesis of nickel monomer (15b). Monomer **15b** was prepared by a procedure identical to that for **15a** except nickel acetate was used in the place of zinc acetate. The monomer was isolated as a red solid (93%) (Found: C, 53.35; H, 6.17; N, 2.91. Calc. for $C_{44}H_{60}I_2N_2O_4Ni$ requires C, 53.19; H, 6.09; N, 2.82%); λ_{max} (CH_2Cl_2)/nm 262 (log ε 6.19), 320 (4.21), 390 (6.59), 473 (2.52); ν_{max}(KBr)/cm^{-1} 2926, 2856, 1608, 1585, 1496, 1463, 1420, 1368, 1279, 1245, 1224, 1186, 1115, 1015, 917, 856, 776; δ_H (300 MHz, $CDCl_3$) 7.57, (s, 2H, C*H*=N), 7.33 (d, *J* = 1.2 Hz, 2H, aromatic C*H*), 6.87 (s, 2H, aromatic C*H*), 6.83 (q, *J* = 1.5, 9.9 Hz, 2H, aromatic C*H*), 6.73 (d, *J* = 8.4 Hz, 2H, aromatic C*H*), 3.90 (d, *J* = 5.4 Hz, 4H, OCH_2), 1.82 (m, 2H, CH_2), 1.42 (m, 32H, CH_2), 0.90 (m, 12H, CH_2); δ_C (75.5 MHz, $CDCl_3$) 164.4, 151.5, 150.4, 136.0, 134.0, 130.5, 124.7, 120.0, 102.5, 97.8, 72.2, 38.4, 32.2, 31.6, 31.2, 30.0, 29.4, 27.3, 23.3, 23.0, 14.4; *m*/*z* (MALDI-TOF) 992.7 (M^+, Calc. 992.2); mp 190–192 °C.

Synthesis of copper monomer (15c). Monomer **15c** was prepared by a procedure identical to that for **15a** except copper acetate was used in the place of zinc acetate. The monomer was isolated as a brown solid (90%) (Found: C, 53.18; H, 6.22; N, 2.94. Calc. for $C_{44}H_{60}I_2N_2O_4Cu$ requires C, 52.94; H, 6.06; N, 2.81%); λ_{max} (CH_2Cl_2)/nm 274 (log ε 3.40), 327 (3.84), 366 (2.96), 416 (5.02); ν_{max}(KBr)/cm^{-1} 2928, 2858, 1606, 1581, 1499, 1461, 1416, 1375, 1275, 1244, 1222, 1182, 1138, 1116, 1057, 1018, 943, 914, 859, 839, 777, 731; *m*/*z* (MALDI-TOF) 997.8 (M^+, Calc. 998.3); mp 128–130 °C.

Synthesis of zinc polymer (4a). Monomers **12a** (0.2007 g, 0.2007 mmol) and **16** (0.1218 g, 0.2007 mmol) were combined in a 100 mL vessel. To these solids were added 10 mL of distilled THF and 4 mL of distilled NH^iPr_2 *via* syringe. The reaction mixture was then degassed by three freeze/pump/thaw cycles. In a glovebox, 5 mol% of $Pd(PPh_3)_4$ and 5 mol% CuI were added. The brown reaction mixture was subsequently freeze/pump/thawed one more time and heated to 75 °C for 24 h. The reaction mixture was then filtered through glass wool and precipitated with 400 mL of MeOH to yield an orange solid. Further purification was performed by precipitating the polymer once from THF into MeOH, and twice into acetone. During the dissolution of the polymer into THF, a very fine beige precipitate would sometimes appear, and was removed by filtration. This procedure yielded polymer **4a** (0.229 g, 85%) as a dark red film (Found: C, 74.22; H, 9.47; N, 2.28. Calc. for $C_{86}H_{129}N_2O_6Zn$ requires C, 76.38; H, 9.61; N, 2.01%); λ_{max} (CH_2Cl_2)/nm 331 (log ε 3.64), 404 (7.60); ν_{max}(KBr)/cm^{-1} 2854, 2203, 1732, 1620, 1506, 1469, 1413, 1379, 1319, 1274, 1216, 1168, 1125, 1025, 881, 853, 833, 750, 721; δ_H (400 MHz, $CDCl_3$, 1% pyridine-d_5). 9–6 (broad, m), 3.3–4.5 (broad), 3.2–0.1 (broad, m); GPC (THF) M_w = 18 700 (M_w/M_n = 1.09).

Synthesis of nickel polymer (4b). Polymer **4b** was prepared by a procedure identical to that for **4a**, starting with monomer **12b**. Precipitations furnished polymer **4b** (84%) as a dark red film (Found: C, 72.44; H, 9.36; N, 2.35. Calc. for $C_{86}H_{129}N_2O_6Ni$ requires C, 76.76; H, 9.66; N, 2.08%); λ_{max} (CH_2Cl_2)/nm 277 (log ε 5.81), 412 (9.33); ν_{max}(KBr)/cm^{-1} 2922, 2204, 1732, 1610, 1494, 1453, 1378, 1274, 1181, 1029, 829, 756; GPC (THF) M_w = 73 600 (M_w/M_n = 1.42).

Synthesis of copper polymer (4c). Polymer **4c** was prepared by a procedure identical to that for **4a**, starting with monomer **12c**. Precipitations furnished polymer **4c** (80%) as a dark red film (Found: C, 76.09; H, 9.64; N, 2.40. Calc. for $C_{86}H_{129}N_2O_6Cu$ requires C, 76.48, H, 9.63; N, 2.07%); λ_{max} (CH_2Cl_2)/nm 279 (log ε 4.55), 412 (9.25); ν_{max}(KBr)/cm^{-1} 2923, 2852, 2204, 1735, 1609, 1586, 1516, 1454, 1414, 1376, 1325, 1274, 1216, 1174, 1124, 1019, 832, 753; GPC (THF) M_w = 33 700 (M_w/M_n = 1.04).

Synthesis of zinc polymer (5a). Polymer **5a** was prepared using a procedure identical to that for **4a**, starting with monomer **15a**. Purification of the polymer was performed by precipitation from THF into hexane twice, and into MeOH twice. Polymer **5a** (77%) was isolated as a dark red solid (Found: C, 72.57; H, 9.37; N, 2.10. Calc. for $C_{86}H_{129}N_2O_6Zn$ requires C, 76.38; H, 9.61; N, 2.01%); λ_{max} (CH_2Cl_2)/nm 341 (log ε 3.10), 430 (6.06); ν_{max}(KBr)/cm^{-1} 2926, 2850, 2206, 1606, 1503, 1467.21, 1413, 1379, 1270, 1215, 1175, 1116, 1018, 986, 867, 723; δ_H (400 MHz, $CDCl_3$, 1% pyridine-d_5). 8.8–8.5 (broad, s), 6.5–7.8 (broad, m) 3.7–4.3 (broad, d), 2.4–0.7 (broad, m); GPC (THF) M_w = 32 800 (M_w/M_n = 1.35).

Synthesis of nickel polymer (5b). Polymer **5b** was prepared by a procedure identical to that for **5a**, starting with monomer **15b**. Precipitations furnished polymer **5b** (72%) as a dark red solid (Found: C, 70.34; H, 8.93; N, 2.10. Calc. for $C_{86}H_{129}N_2O_6Ni$ requires C, 76.76; H, 9.66; N, 2.08%); λ_{max} (CH_2Cl_2)/nm 277 (log ε 4.74), 402 (3.43); ν_{max}(KBr)/cm^{-1} 2927, 2852, 2201, 1732, 1604, 1494, 1468, 1275, 1217, 1029, 866, 722; δ_H (400 MHz, $CDCl_3$, 1% pyridine-d_5). 8.2–6.6 (broad, m), 3.5–4.5 (broad), 3.2–0.4 (broad, m); GPC (THF) M_w = 60 400 (M_w/M_n = 1.43).

Synthesis of copper polymer (5c). Polymer **5c** was prepared by a procedure identical to that for **5a**, starting with monomer **15c**. Precipitation furnished polymer **5c** (90%) as a dark red solid (Found: C, 70.80; H, 8.89; N, 2.01. Calc. for $C_{86}H_{129}N_2O_6Cu$ requires C, 76.48, H, 9.63; N, 2.07%); λ_{max} (CH_2Cl_2)/nm 276 (log ε 3.85), 344 (3.27), 448 (7.00); ν_{max}(KBr)/cm^{-1} 2913, 2866, 2204, 1734, 1610, 1523, 1490, 1464, 1379, 1273, 1186, 1142, 1113, 1013, 984, 872, 825, 791, 721; GPC (THF) M_w = 63 200 (M_w/M_n = 1.25).

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