

Synthesis of soluble conjugated metalloporphyrin polymers with tunable electronic properties

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New linear conjugated porphyrin polymers are synthesized by a palladium-catalyzed cross-coupling reaction of [5,15-bis(ethynyl)-10,20-bis(mesityl)porphyrin]zinc and diiodobenzene derivatives; enhanced solubility of the conjugated porphyrin polymers is achieved by attachment of long alkyl ether or dialkyl amide groups to the aryl moiety, resulting in unambiguous characterization by ^1H NMR, IR, GPC, UV-VIS and fluorescence spectroscopy; in addition, the introduction of alkyl ether (electron donor) or dialkyl amide (electron acceptor) results in significant modulation of the electronic properties of the conjugated porphyrin polymers owing to strong electronic coupling.

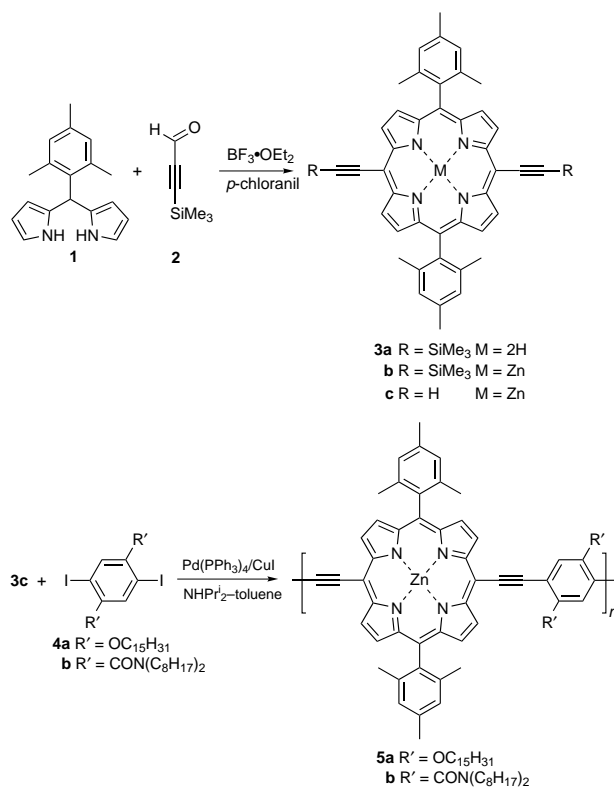
Conjugated porphyrin polymers and oligomers are an attractive new class of materials with potential applications in the fields of electronics, optical devices, sensors and solar energy conversion.^{1–7} Although the synthesis of a wide variety of porphyrin dimers or oligomers *via* the building block approach is well developed, relatively few soluble conjugated porphyrin polymers have been studied.¹ Anderson *et al.* have synthesized a soluble, linear conjugated *meso*-butadiyne-linked porphyrin polymer with long alkyl chains on the porphyrin periphery. The polymer exhibits an unusually high susceptibility $\chi^{(3)}$ and strong electronic communication as well as electronic absorption in the near IR.^{1a} However, the electronic tuning of the *meso*-butadiyne-linked porphyrin polymers is synthetically challenging. Therien and DiMugno also reported the synthesis of poly(diethynylaryl porphyrin) with limited characterization.^{1b} Recently, we synthesized a series of soluble *meso*-phenylporphyrin-based polymers with tunable electronic and photophysical properties.^{5,6} Unfortunately, the electronic communication along the polymer backbone was limited due to steric interactions between the phenyl *ortho* proton and the porphyrin β -hydrogen, resulting in a large dihedral angle between the porphyrin ring and the phenylenevinylene unit.^{5–8} We present here a modified approach to soluble and fully conjugated porphyrin polymers with tunable electronic and optical properties that builds on previous efforts.

The design and synthesis of the new conjugated porphyrin polymers and their precursor porphyrin monomers are outlined in Scheme 1. The *meso*-(mesityl)dipyrromethane **1** was synthesized from pyrrole according to a literature procedure.⁹ Condensation of **1** with (trimethylsilyl)propynal **2** gives trimethylsilyl-protected porphyrin **3a** in 30% yield.¹⁰ Metallation of porphyrin **3a** with $\text{Zn}(\text{OAc})_2$, followed by deprotection of the terminal acetylene with tetrabutylammonium fluoride leads to **3c**. Porphyrin polymers **5a** and **5b** were synthesized from palladium-catalyzed cross-coupling reaction of porphyrin monomer **3c** and the corresponding diiodoaryl compounds **4a** or **4b**¹¹ in 90% yields.[†] The high solubility of the polymers was achieved by attaching long pendant chains to the aryl units. The mesityl substituents on the porphyrin moiety also contribute to the solubility of the polymers.¹²

^1H NMR spectra of the polymers in CDCl_3 demonstrated the expected polymer structure (Scheme 1). For polymer **5b**, two broad peaks at δ 9.7 and 8.8 are observed and assigned to the β -pyrrole protons of the porphyrin subunits. The resonance of

the two aromatic protons corresponding to aryl units appears at δ 8.1, much further downfield from δ 7.55 as seen in monomer **4b**. No signal was observed near δ 4.1 for an acetylenic proton, supporting the formation of the diethynylaryl-linked porphyrin polymer. Also no absorbance was observed at 2091 cm^{-1} in the IR spectrum due to acetylene end-groups, consistent with ^1H NMR results. The formation of the ethynyl link was further confirmed by absorbance at 2184 cm^{-1} in the IR spectrum. The NMR and IR data suggest a high degree of polymerization in these materials. The average molecular mass was determined by GPC to be $M_w = 5.17 \times 10^4$, $M_n = 2.45 \times 10^4$, using polystyrene standards. Attempts at using multi-angle light scattering to independently determine molecular mass were unsuccessful due to competitive absorption.

The insertion of a triple bond between the porphyrin and aryl subunits was expected to enhance electronic interaction in the main polymer chain as demonstrated previously for dimeric systems.⁸ Fig. 1(a) shows the absorption spectra of polymers **5a** and **5b** compared with the monomer **3c**. In both cases, the porphyrin polymers exhibit dramatic red-shifts and broadening in both the B- and Q-type transition bands in comparison to porphyrin monomer **3c**. This would indicate strong electronic interactions along the conjugated porphyrin backbone.^{1–3}



Scheme 1 Synthesis of conjugated porphyrin polymers and their precursors

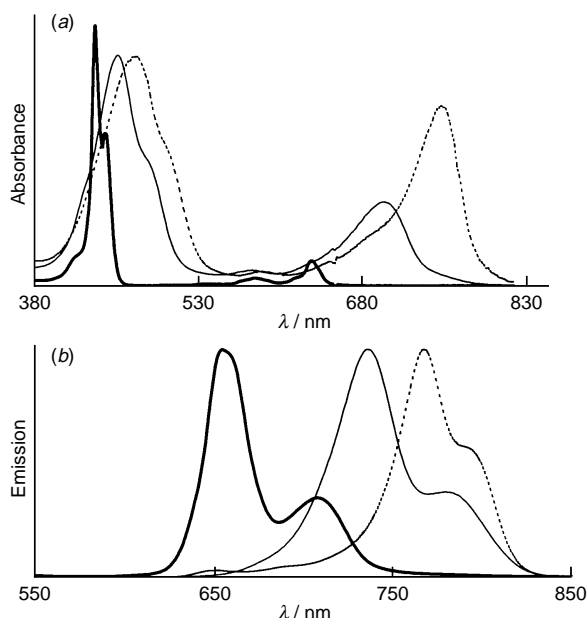


Fig. 1 (a) UV-VIS absorption spectra of monomer **3c** and polymers **5a** and **5b** in THF solution and (b) emission spectra of monomer **3c** and polymers **5a** and **5b** in THF solution (465 nm excitation); (—) monomer **3c**, (---) polymer **5a**, (· · ·) polymer **5b**

In the presence of strong electronic coupling, introduction of the aryl units into the porphyrin polymer main chain allows for facile modification of the electronic properties through the pendant aryl substituent. The observed decrease in absorption energy on going from polymer **5b** to **5a** is consistent with the electron donating character of the ether alkyl substituent and electron withdrawing character of the dialkyl amide substituent on the aryl 'bridge' units. Cyclic voltammetry measurements in 0.5 M tetrahydrofuran and dichloromethane solution show a shift in the oxidation potential from 0.94 to 0.75 V vs. SCE on going from polymer **5b** to **5a**. As compared to the monomer electrochemical oxidation at 0.95 V vs. SCE under similar conditions, substantial broadening in ΔE_p was observed. The observed modulation of ground-state electronic properties of the polymer suggests high electron coupling along the conjugation of the polymer backbone.

The emission spectra of the polymers and the monomer are shown in Fig. 1(b). Both polymers exhibit significant red-shifts in comparison to that of the monomer. Polymer **5a** displays a larger red shift than polymer **5b**, consistent with the electronic absorption spectra. The emission lifetimes of polymers **5a** and **5b** were 0.92 and 1.1 ns respectively, which is shorter than that of the porphyrin monomer (2.5 ns) measured in THF at room temp. The fluorescence quantum yields of the monomer and polymers **5a** and **5b** are 0.071, 0.028 and 0.069, respectively. The decrease in emission lifetime and the observed shifts in the emission spectra upon bridge substitution are also consistent with increased electronic delocalization in the polymer excited state relative to the *meso*-phenylene vinylene linked porphyrin polymers reported previously.⁵ Enhanced exciton mobility in these soluble one-dimensional systems would also be consistent with these fluorescence data, but more information is necessary before this mechanism can be confirmed.

The electronic absorption and emission spectra of both polymers also display significant solvent dependence. The emission maximum shifts to lower energy on going from chloroform (704 nm) to *n*-butylamine (741 nm). This is related to the well known axial complexation ability of the central metal cation of the porphyrin toward different solvent ligands.¹³ The electron-donating ability of the solvent ligand increases as the

solvent basicity increases. Complexation of the solvent to the metal cation results in increased electron density on the porphyrin units. It is important to note that either an increase in the electron density of the diethynyl aryl unit through pendant groups or the porphyrin units through axial solvation leads to a red shift in the absorption and emission bands.

In summary, we have developed a modified approach to synthesizing a family of fully conjugated, soluble porphyrin polymers in which the porphyrin units are connected by the diethynylaryl group. The porphyrin monomers are easily synthesized, and the high solubility of the polymers in common organic solvents allows routine manipulation, chemical characterization and spectroscopic analysis. The ground and excited state electronic properties suggest enhanced delocalization which can be fine-tuned through the structural modification of the more synthetically accessible aryl bridge units, rather than by direct modification of the porphyrin moiety. The unique coordinating ability of the central metal cation, combined with the high electronic coupling and fluorescence in the polymers, may provide an opportunity to develop optical sensors based on this family of conjugated porphyrin polymers.¹³

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Footnotes and References

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† Preparation of polymers (typical procedure): under an atmosphere of argon, diisopropylamine (1.5 ml) in THF (3 ml) was added to a 15 ml Schlenk flask containing porphyrin **3c** (0.05 g, 0.0076 mmol), diiodobenzene **4a** or **4b** (0.076 mmol), CuI (5 mg) and Pd(PPh₃)₄ (6.5 mg). This mixture was refluxed for 24 h and then subjected to CHCl₃/H₂O. The combined organic phase was washed with NH₄OH (50%), H₂O and dried over MgSO₄. Most of the solvent was evaporated in under vacuum and the concentrated solutions poured into MeOH. The polymer precipitated as a green solid in 90% yield.

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