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Amino-Substituted *para*-Phenylenevinylenes (PPVs) as Platforms for Fluorescent Sensing Materials

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Summary: Soluble *para*-phenylenevinylenes (PPVs) with amino side groups and different spacers have been synthesized. Photophysical properties showed that these compounds emitted light in blue region when dissolved in methanol. They have been designed in order to be platforms for attaching different functional groups to the amino units. Molecule **5** was a model compound which showed a quantum efficiency of 52% in methanol. Different spacers were added to the model compound to yield molecules **6** and **7**. The preliminary experiment showed that molecule **5** can interact with various metal ions in solution phase. The interaction was observed by the changes of fluorescent emission intensity of the molecule. This molecule will be further functionalized to be more specific in binding certain metal ions.

Keywords: conjugated polymer; fluorescence; quenching; sensor; synthesis

Introduction

Conjugated oligo- and poly-*p*-phenylene vinylenes (PPVs) are well known as light emitters due to the delocalization of electrons along the main chains. These molecules are durable, cheap, and easy to process. With all these properties, PPVs have drawn researchers attention to extensively apply them as emissive layers in organic light-emitting diodes (OLEDs). Many structural designs have been tailored in order to improve the efficiencies and lifetime of the devices. The luminance (brightness) of OLEDs with PPV-based molecules as emissive layers has already reached over 3000 cd/m^2.[1,2] Moreover, when carbon nanotubes were applied to the system, the luminance was increased tremendously.[3] Even though PPVs have been in the spotlight for quite a long time, there are still various ways for modifying and using them. The most popular modification is to substitute different functional groups into the backbone. Moreover, the polymeric version of PPVs can be co-polymerized with some other polymers to obtain multi-functional systems. Conjugated units, for example, fluorene[4,5] and naphthalene[6] have also been directly incorporated into the main PPV chain. One promising application of PPVs is being fluorescent sensing materials. By designing suitable binding units, PPVs could be used for detecting various kinds of analytes.

Metal ions-contamination in food and environment extensively affects human health due to their toxicity.[7–9] These metals are typically released from industrial factories into rivers. The water is then used for plantation and household living, so these contaminants are absorbed by human and animals. In order to prevent the problem, the metal ions have to be detected before hands. Various methods and instruments have been applied to determine the metal ions content. The conventional methods for analyzing heavy metals are techniques which rely on big and expensive instruments such as atomic absorption spectroscopy (AAS)[10–12] or inductively coupled plasma optical emission spectrometry (ICP-OES).[13–14] These techniques

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are highly sensitive and reliable but require a complicated sample-preparation process and cannot be used outside the laboratory. According to this limitation, we intended to develop materials and protocols for a less-complicated metal-detecting device.

This article described the synthesis of amino side-chain *p*-phenylenevinylene trimer and its derivatives, photophysical properties, and fluorescence quenching phenomenon. Amino PPV trimer was designed in order to be platform for attaching other functional units to the PPV trimer. Metal ions sensing capability of the platform molecule was preliminary determined by observing the changing of fluorescent emission intensity in solutions.

Materials and Methods

All commercially available chemicals were used as received. Acetonitrile was HPLC grade. Tetrahydrofuran (THF) and dimethyl formamide (DMF) were extra-dry grade packed with molecular sieves and rubber septa. ^{1}H NMR spectra were obtained using Bruker 300 MHz spectrometer. UV-Vis and fluorescence spectra were measured using Perkin Elmer Lambda 650 and Perkin Elmer LS 55 spectrometers, respectively. Gel-permeation chromatography was done by Waters 717 system.

Synthesis of the Compounds

Molecule 5

Into a dry flask under a nitrogen atmosphere, 3,4,5-trimethoxystyrene (2.00 mmol, 0.39 g), 1,4-bis[2-(2-phthalimido)ethoxy]-2,5-diiodobenzene (1.00 mmol, 0.71 g), tri(*o*-tolyl)phosphine (0.48 mmol, 0.15 g), and palladium diacetate (0.035 mmol, 0.0078 g) were added. Anhydrous dimethylformamide (12.5 mL) was added as a solvent. Triethylamine (5.02 mmol, 0.7 mL) was added when the temperature reached 80 °C. The reaction mixture was then stirred at 100 °C for 3 days. The reaction was allowed to cool, then dichloromethane was added, and the resultant precipitate was filtered. The solid was washed with hexanes and further purified by column chromatography to yield a yellow powder (0.40 g, 48%). Hydrazine hydrate (98%) (0.24 mmol, 1 mL) was added to the suspension of the obtained yellow powder (0.24 mmol, 0.20 g) in absolute ethanol (1 mL). The reaction mixture was stirred at room temperature overnight, then neutralized by addition of 5 M aqueous hydrochloric acid. Next, 2 M aqueous sodium hydroxide was added, and the solution extracted with dichloromethane. The organic layer was dried and evaporated, to yield the crude product. After purification by column chromatography, the product was isolated as a bright yellow powder (0.086 g, 63%) ^{1}H NMR ($CDCl_3$): δ 3.15 (t, 4 H, $J = 4.0$ Hz), 3.80 (d, 2 H, $J = 2.0$ Hz), 3.85(s, 6 H), 3.90 (s, 12H), 4.09 (t, 4 H, $J = 4.0$ Hz), 6.74 (s, 4 H), 7.05 (d, 2H, $J = 16.0$ Hz), 7.12 (s, 2 H), 7.29 (d, 2 H, $J = 16.0$ Hz). UV-vis (methanol, λ_{max}): 386 nm. Photoluminescence (methanol, λ_{exc}= 365 nm): $\lambda = 439$ nm (max).

Molecule 6

Into a dry flask under a nitrogen atmosphere, 1,2-bis(4-vinyl-2,6-dimethoxyphenoxy) hexane (1.02 mmol, 0.45 g), 1,4-bis[2-(2-phthalimido)ethoxy]-2,5-diiodobenzene (1.02 mmol, 0.72 g), tri(*o*-tolyl)phosphine (0.26 mmol, 0.08 g), and palladium diacetate (0.027 mmol, 0.006 g) were added. Anhydrous dimethylformamide (24 mL) was added as a solvent. Triethylamine (10.76 mmol, 1.5 mL) was added when the temperature reached 80 °C. The reaction mixture was then stirred at 100 °C for 3 days. The reaction was allowed to cool, then poured into a mixture of 50 mL of methanol and 5 mL of 2 M aqueous HCl, and the resulting precipitate was filtered. The solid was purified by column chromatography (silica, chloroform) to yield a yellow powder (0.28 g, 28%). Hydrazine hydrate (98%) (0.28 mmol, 1.17 mL) was added to a suspension of the obtained yellow powder (0.28 mmol, 0.27 g) in absolute ethanol (1 mL). The reaction mixture was stirred at room temperature overnight, then neutralized by addition of 5 M aqueous hydrochloric acid. Next, 2 M aqueous sodium hydroxide was added and the solution was extracted with dichloromethane. The organic layer was dried and evaporated to yield a yellow powder (0.16 g, 92%). ^{1}H NMR (DMSO-d_6): δ 1.48(m, 4 H), 1.76 (m, 4 H), 2.88 (m, 4 H), 3.72-4.03 (m, 20 H), 6.48 (m, 4 H), 6.87 (m, 2 H), 7.27-7.41(m, 4 H) UV-vis (methanol, λ_{max}): 347 nm. Photoluminescence (methanol, λ_{exc}= 365 nm): $\lambda = 442$ nm (max).

Molecule 7

Into a dry flask under a nitrogen atmosphere, **4** (2.91 mmol, 0.38 g), **1** (2.92 mmol, 2.06 g), tri(*o*-tolyl)phosphine (0.72 mmol, 0.22 g), and palladium diacetate (0.052 mmol, 0.012 g) were added. Anhydrous dimethylformamide (15 mL) was added as a solvent. Triethylamine (7.89 mmol, 1.1 mL) was added when the temperature has reached 80 °C. The reaction mixture was then stirred at 100 °C for 6 days. The reaction was allowed to cool and poured into a mixture of 200 mL of methanol and 20 mL of 2 M aqueous HCl. The resultant precipitate was filtered to yield an orange brown residue which was reacted with□ hydrazine hydrate (98%) (1.27 mmol, 3.05 mL) in absolute ethanol (2 mL). The reaction mixture was stirred at room temperature overnight and neutralized by addition of 5 M aqueous hydrochloric acid. Next, 2 M aqueous sodium hydroxide was added and the solution was extracted with dichloromethane. The organic layer was dried and evaporated to yield a yellow solid (0.50 g, 86%). ^{1}H NMR (DMSO-d_6): δ, 3.01 (m, 4 H), 4.06 (m, 4 H), 7.12-7.58 (m, 10 H) UV-vis (methanol, λ_{max}): 339 nm. Photoluminescence (methanol, λ_{exc}= 365 nm): $\lambda = 432$ nm.

Photophysical Properties

Relative quantum efficiencies (ϕ) were calculated using quinine sulfate dihydrate in 0.1 M sulfuric acid as a reference ($\phi = 0.546$), at an excitation wavelength (λ_{exc}) of 365 nm. The quantum efficiency calculations were done by using the equation [19]

$$\phi_s = \phi_{ref}\left(\frac{I_s}{I_{ref}}\right)\left(\frac{A_{ref}}{A_s}\right)\left(\frac{n_s}{n_{ref}}\right)^2 \qquad (1)$$

where I is the integral of emission spectrum, A is the absorption at the specific wavelength, *n* is the refractive index of the solvent.

Responses to Metal Ions

The model compound **5** was tested the response to the external analytes. Trimer **5** was dissolved in acetonitrile at the concentration of 8.6×10^{-7} M for testing responses to metal ions. Solutions of zinc(II)acetate, manganese(II)acetate, nickel(II)acetate, cobalt(II)acetate, copper chloride, cadmium(II)acetate, lead(II)actatate, sodium chloride, and lithium chloride were also prepared in acetonitrile at the concentration of around 10^{-4} M. The solutions of the metal ions were added into the solution of molecule **5**; then the interaction was observed by fluorescence spectrometer.

Results and Discussions

A group of 3 amino-substituted *p*-phenylenevinylenes has been synthesized through Heck cross-coupling reaction. The primary amines were introduced to the PPV units by hydrazinolysis of the phthalimido intermediates. Trimer **5** was synthesized as a model compound of the amino-substititued PPVs.[15] It was obtained as a bright yellow powder which was soluble in various organic solvents. Absorption and emission spectra of trimer **5** in methanol were shown in Figures 2 and 3, respectively. The molecule emitted light in blue region. The fluorescent quantum efficiency was determined relatively to quinine sulfate to be 52% in methanol.

Molecules **6** and **7** were designed to contain 2 different types of spacers which were aliphatic and aromatic units, respectively. Gel-permeation chromatography (GPC), with polystyrene as a standard, indicated the molecular weight of 1800 g/mol

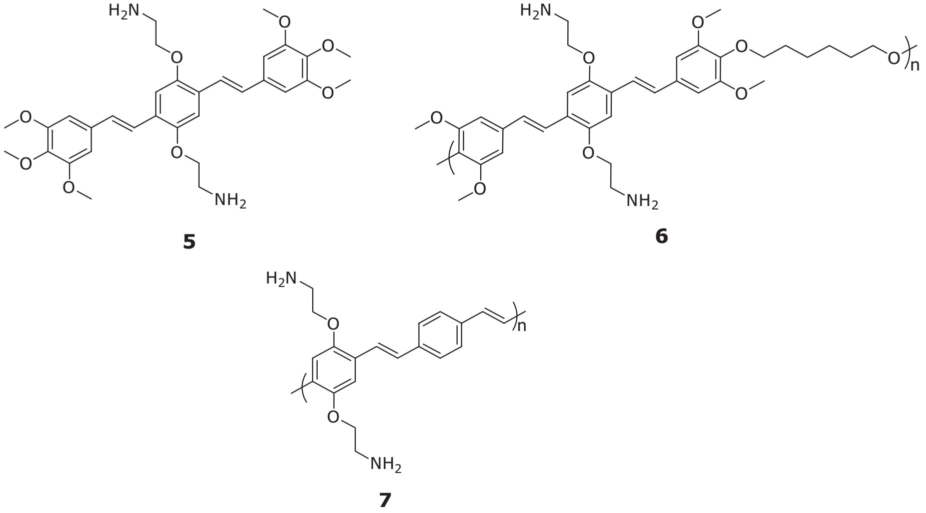
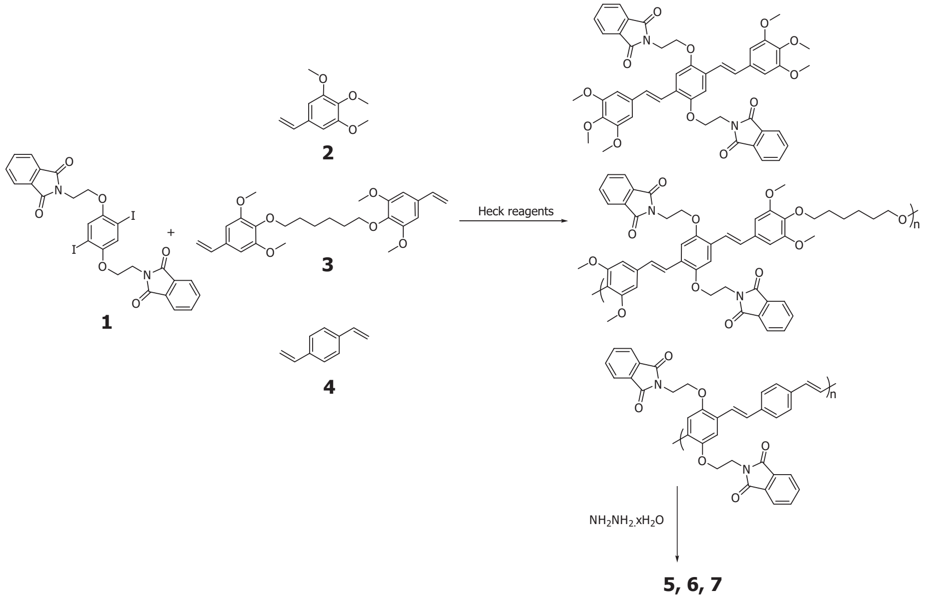


Figure 1.
Amino-substituted *p*-phenylenevinylenes synthesized in this work.

for molecule **6** and 1350 g/mol for molecule **7**. The quantum efficiency of molecule **6** was calculated to be 48% in methanol which was comparable to that of trimer **5**. Molecule **7**, although soluble in methanol, did not result in high quantum efficiency; it was calculated to be 29%. The lower quantum efficiency resulted from non-radiative processes during the photo-excitation.

Of all the molecules synthesized, the trimer **5** turned out to be the best one with which to work. The synthesis was very straight forward and the quantum efficiency



Scheme 1.
Routes for preparing molecules **5**, **6**, and **7**.

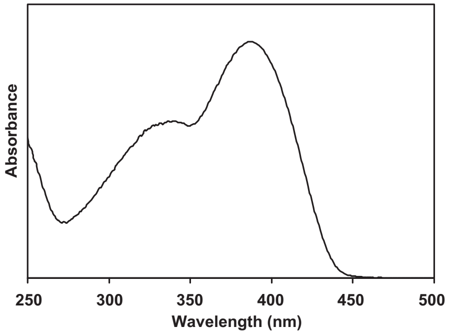


Figure 2.
Absorption spectrum of trimer **5**.

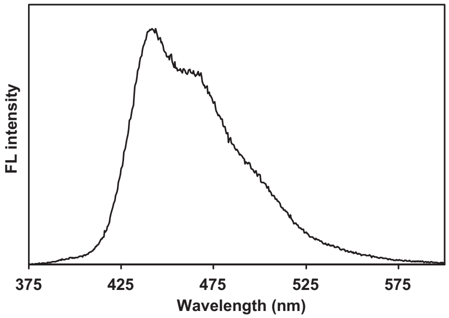


Figure 3.
Emission spectrum of trimer **5**.

was high enough to make it easy to detect changes due to interactions. It was chosen over molecules **6** and **7** for functionalization to detect certain analytes.

Fluorescent Quenching of Trimer 5

Since the trimer **5** will be used as a fluorescent platform for developing metal ion-detecting systems, the molecule itself was tested for interaction with some metal ions in order to observe the quenching pattern. Figure 4 displays the quenching effect on fluorescent intensity of trimer **5** by various metal ions in acetonitrile. The strong fluorescent emission intensity of pure trimer **5** (8.6×10^{-7} M) changed upon the addition of the metal ion solutions ($\sim 10^{-4}$ M).

The comparison of the fluorescent emission intensities at 431 nm (λ_{max} in CH_3CN) is shown in Figure 5. The quenching effects can be generally categorized into four groups: no quenching in cases of Zn(II), Mn(II), Li(I), and Na(I); slight quenching in cases of Cd(II) and Pb(II); moderate quenching in case of Co(II); and strong quenching in cases of Ni(II) and Cu(I). The selectivity toward Ni(II) and Cu(I) could be explained as both metal ions are azaphiles so they promptly reacted with

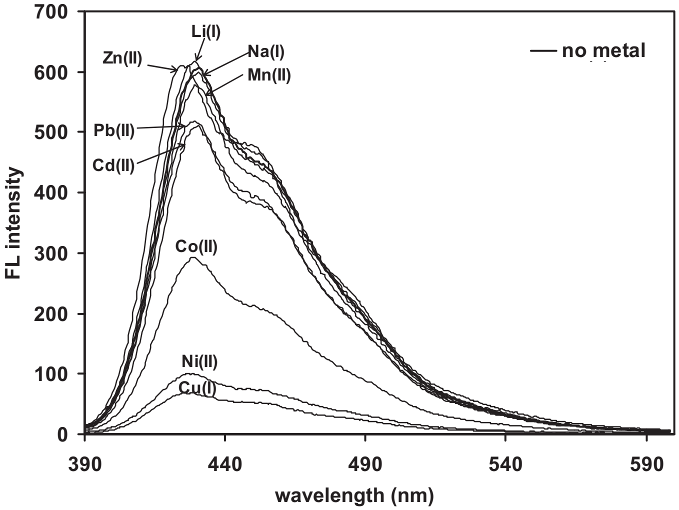


Figure 4.
Fluorescent emission spectra of trimer **5** upon the addition of metal ion solutions.

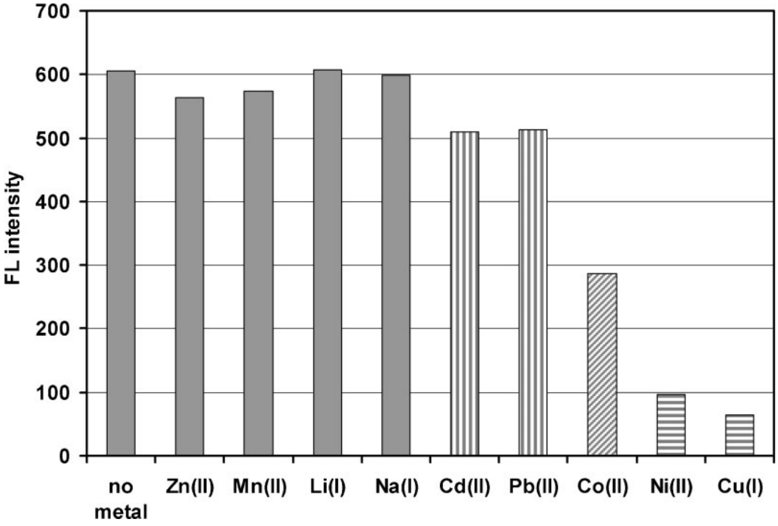


Figure 5.
Comparison of the fluorescent emission intensities at 431 nm.

nitrogen atoms of the trimer **5**. The decreased fluorescent intensity was attributed to photo-induced electron-transfer between the electron-rich amino side-chain trimer and the metal ions. The excited electrons from the trimer were tranferred to the electron-deficient metal ions so they can not return to the ground state and emit light. Nevertheless, no shift in emission wavelength was observed upon the exposure.

From the observations, the amino-substituted PPV trimer is considered as a promising platform molecule for use as fluorescent sensor. The responses to some metal ions seemed to be satisfying; however, further functionalization has to be applied to the molecule in order to increase the specificity to certain metal ions.

Conclusion

Three structurally related oligo *p*-phenylenevinylenes with amino side-groups have been synthesized and characterized. The molecules emitted light in blue region when dissolved in methanol and/or water. The amino groups were introduced to the conjugated back-bone in order to be sites for attaching fuctionalities. These molecules will be used as platforms for developing fluorescent sensors. The model compound **5** gave the highest quantum efficiency among the series. The preliminary experiment showed that trimer **5** has potential to be used as fluorescent sensor for the detection of metal ions in solution phase. The process of developing fluorescent sensors based on these molecules is still under investigation.

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