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Novel Poly(*p*-phenylenevinylene)s with a Phenylazomethine Dendron as a Metal-Collecting Site

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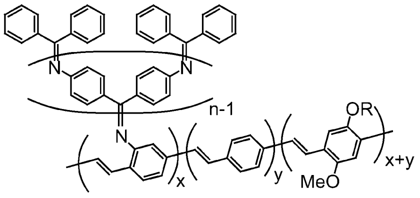
ABSTRACT



DPA-PPVs

Novel poly(*p*-phenylenevinylene)s (PPVs) with a dendritic phenylazomethine (DPA) as a metal-collecting site were synthesized via the Heck reaction by filling the coordination site of DPA moiety via complexation with rare earth metal ions.

Functional π-conjugated polymers have inspired various applications such as organic light-emitting diodes (OLEDs)[1] and photocells.[2] Recently, various substituents on the PPVs have been introduced, providing additional properties such as magnetic[3] and charge-transporting[4] substituents.

Recently, we reported hole transport materials with a phenylazomethine moiety as a metal-collecting unit that resulted in a higher EL efficiency simply by complexation with a metal ion.[5] To develop a new type of light-emitting materials, we have synthesized novel poly(*p*-phenylenevinylene)s (**DPA-PPV**s) with the phenylazomethine dendron as the metal-collecting site. We found a novel synthesis of PPV derivatives with a bulky group having coordination sites such as phenylazomethine dendrons, which inhibit the coupling by trapping catalysts by filling the coordination sites with rare earth metal ions.

In general, two different synthetic routes can be used to produce dendron-functionalized polymers. The first route utilizes a polymer backbone with anchor groups to either convergently or divergently attach a dense sequence of dendrons (grafting route).[6] The second utilizes monomers already having dendrons, which are allowed to undergo polymerization (macromonomer route).[7] We adopted the macromonomer route to avoid the intrinsic problems of grafting, such as achieving complete coverage of the polymer backbone with dendrons, the solubility of the polymer

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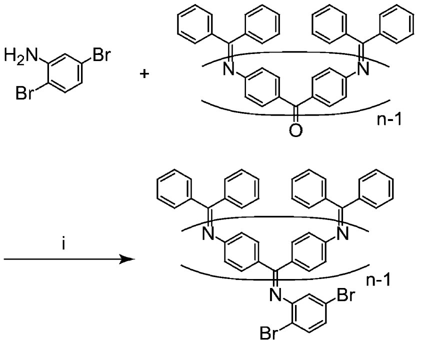
backbone during the second reaction (grafting reaction), and purification of the product from the reaction mixture. We investigated the reaction conditions for the model compounds. The macromonomers (**DPA-Br$_2$ G*n***, $n = 1-3$) were obtained by dehydration between excess 2,5-dibromoaniline and the corresponding phenylazomethine dendrons[8] (Scheme 1). In our study, 2,5-substituted phenylazomethine dendrimers were obtained in relatively low yields (<50%) as a result of steric hindrance between the bulky dendrons and substituents at the core.[9] We have refined the dehydration conditions, utilizing a large excess of 2,5-dibromoaniline, and succeeded in preparing the corresponding macromonomers in very high yields (>90%).

Scheme 1. Synthesis of **DPA-Br$_2$ G*n***[a]

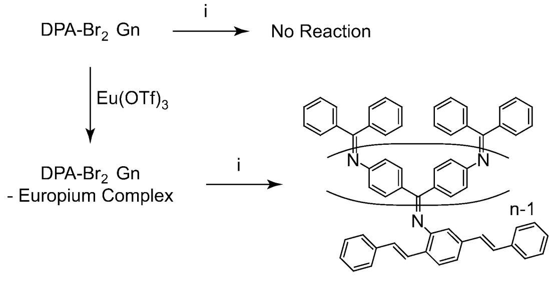


DPA-Br$_2$ Gn (n=1-3)

[a] Reagents and conditions: (i) $TiCl_4$, DABCO, PhCl.

We then examined the palladium-catalyzed Heck reactions for the polymerizations.[1d,7a,10] The macromonomers were simply allowed to react with styrene, but the corresponding compounds were not obtained under the normal synthetic conditions. This result suggested that the phenylazomethine dendron unit acted as a metal-collecting site and a catalytic amount of palladium was trapped and prohibited the oxidative insertion into the monomer. The complexed macromonomers with metal ions were then employed to avoid the deactivation of the palladium catalyst by complexation and reacted with styrene.[11] The Heck reaction successfully proceeded and produced the reaction compounds (**DPA-DSB G*n***) as confirmed by ^1H and ^{13}C NMR analyses (Scheme 2). $Eu(OTf)_3$ in the reaction mixture was removed by silica gel column chromatography. However, the reaction of **DPA-Br$_2$ G3** does not proceed because of the incomplete capping of the metal-collecting sites and the inhibition of the catalyst.[12] In the same way, we can apply this to other palladium-catalyzed reactions such as the Suzuki coupling and Sonogashira coupling reactions by initially complexing with rare earth metal ions.[13]

Scheme 2. Synthesis of **DPA-DSB G*n***[a]



DPA-DSB Gn (n=1, 2)

[a] Reagents and conditions: (i) styrene, $Pd(OAc)_2$, $P(o\text{-tol})_3$, $(i\text{-}Pr)_2NH$, dioxane.

The addition of $SnCl_2$ to a chloroform/acetonitrile solution of **DPA-DSB G*n*** ($n = 1-3$) resulted in complexation with a stepwise spectral change, similar to that for the previously reported phenylazomethine dendrimers.[5a,9,14] During the addition of $SnCl_2$, the solution color of **DPA-DSB G*n*** changed from light to a deeper yellow. We observed that the complexation was complete within 10 min by the spectral change after the addition of $SnCl_2$, that is, the complexation equilibrium is reached within at least several minutes. Using UV−vis spectroscopy to profile the complexation, changes in the position of the isosbestic points were observed, indicating that the complexation proceeds not randomly but stepwise. This result suggests that three different complexes are successively formed during the $SnCl_2$ addition.

Typically, the spectra of **DPA-DSB G2** gradually changed, with an isosbestic point at 337 nm up to the addition of 1 equiv of $SnCl_2$ (Figure 1). The isosbestic point then shifted upon the further addition of $SnCl_2$ and appeared at 339 nm

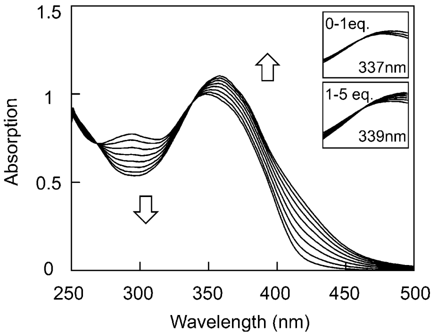


Figure 1. UV−vis spectra changes of **DPA-DSB G2** upon stepwise addition of $SnCl_2$ in $CH_3CN/CHCl_3 = 1/2$. (Insert) Enlargements showing isosbestic points.

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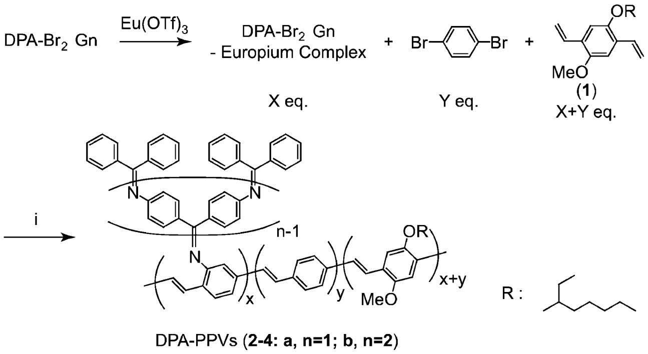
(11) Eu^{3+} ion was selected for the complexation with the phenylazomethine unit in the reaction because of the electrochemical stability.

with additional $SnCl_2$.[15] Overall, the number of added equivalents of $SnCl_2$ required to induce a shift agreed with the number of imine sites present in the different layers of **DPA-DSB**. The titration results suggest that the complexation proceeds in a stepwise fashion from the core imines to the terminal imines of **DPA-DSB G2**. A similar stepwise complexation was also observed with **DPA-DSB G1** and **G3**.[16]

A similar reaction was developed for the polymerizations with 1-methoxy-4-(2-ethylhexyloxy)-2,5-divinylbenzene (**1**) as shown in Scheme 3. Without a spacer in the reaction mixture, the polymerization occurred very slowly; the reaction of **DPA-Br$_2$ G1** required a very long time, while that of **DPA-Br$_2$ G2** did not result in any polymers not soluble in methanol. We employed *p*-dibromobenzene as a spacer to reduce the rate of the DPA moiety in the reaction mixture. However, the polymerization of **DPA-Br$_2$ G3** does not proceed because of the cooperative effect of incomplete capping of the metal-collecting sites and their steric hindrance, considering the reaction time for the polymerization. The Heck reaction succeeded and yielded the corresponding polymer (**DPA-PPV G*n***) with higher molecular weights (M_w's). $Eu(OTf)_3$ in the reaction mixture was removed by Soxhlet extraction. The content of the DPA unit in the polymer was determined by profiling the amount of benzophenone produced via the hydrolysis of the polymers in the presence of sulfuric acid. These polymers are soluble in common organic solvents such as tetrahydrofuran (THF), chloroform, and toluene. The M_w's of these polymers were determined using gel permeation chromatography equipped with a light-scattering detector and are shown in Table 1.

Scheme 3. Synthesis of **DPA-PPVs**[a]



[a] Reagents and conditions: (i) (a) $Pd(OAc)_2$, $P(o\text{-tol})_3$, $(i\text{-Pr})_2NH$, NMP, (b) styrene.

Table 1. Characterization of **DPA-PPV**s

	X/*Y*	yield (%)	*x*/*y*[a]	M_w[b] (kDa)	PDI[c]
2a	1/0	47	1/0	9.8	1.2
3a	1/3	62	1/3	13.8	1.5
4a	1/7	68	1/8	37.0	3.1
2b	1/0	0[d]			
3b	1/3	48	1/7	26.7	1.2
4b	1/7	58	1/16	23.7	1.1

[a] Determined by profiling the amount of benzophenone yielded via the hydrolysis reaction with sulfuric acid. [b] Determined using gel permeation chromatography equipped with a light-scattering detector in THF. [c] PDI: M_w/M_n. [d] Insoluble part in methanol.

These results suggest that the steric hindrance between the DPA unit and **1** was reduced by introducing *p*-dibromobenzene as a spacer. Indeed, the polymerization profiles detected by preparative scale gel permeation chromatography (preparative GPC) revealed that the lower reaction rate of **DPA-Br$_2$ G2** was estimated compared to that of **DPA-Br$_2$ G1** on the basis of the degree of steric hindrance between the DPA unit and **1**.

UV−vis and fluorescent spectra of the polymer solution in chloroform (**3a**, **4a**, **3b**, and **4b**) are shown in Figure 2.

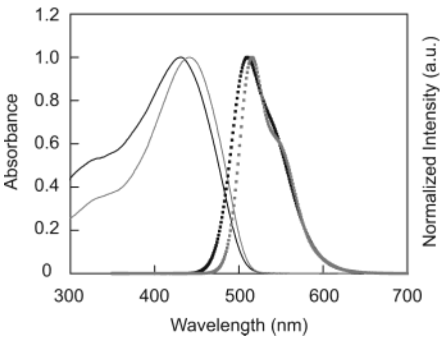


Figure 2. UV−vis (—) and fluorescence (· · ·)[17] spectrum of **DPA-PPV G1**: (black) **3a**, (gray) **4a** in chloroform.

As shown here, these polymers show the absorption band around 435 nm attributed to the $\pi-\pi^*$ transition of the main polymer chain, whereas DPA has the absorption band around 300−425 nm. As well, these polymers readily showed a relatively strong emission around 510 nm derived from the PPV moiety compared with other phenylazomethine dendrimers and are expected for the application for OLEDs.

With the addition of $SnCl_2$ to the chloroform solution of the **DPA-PPV**s, the UV spectrum changed similarly to that of the model compounds, suggesting that the phenylazo-

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(12) Eu^{3+} could fill the metal-collecting sites of DPA G3 unit in dichloromethane/acetonitrile 1/1 solution as published previously (ref 13a). However, these reactions were performed in dioxane or NMP with a larger polarity. Actually, in case of the reaction of **DPA-Br$_2$ G3**, a large amount of uncomplexed $Eu(OTf)_3$ existed in the reaction mixture as an insoluble part in the solvent during the reaction, although $Eu(OTf)_3$ equimolar to the phenylazomethine unit was added.

(13) See Supporting Information for details.

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(15) The complexation could not finish adding the equal molecular amount of $SnCl_2$ to the stoichiometry of the imine groups. This is due to the lower equilibrium constant, which is about 10 times smaller for **DPA-DSB G1**. The equilibrium constant was estimated from the titration curve for complexing **DPA-DSB G1** with $SnCl_2$ (see Supporting Information).

(16) **DPA-DSB G3** was synthesized via the grafting route (see Supporting Information).

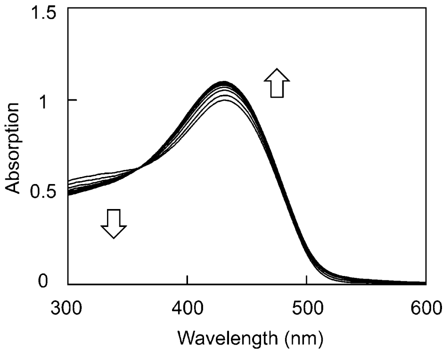

Figure 3. UV−vis spectra changes of **3b** upon stepwise addition of $SnCl_2$ in $CHCl_3$.

methine group in the polymer is also capable of assembling metals (Figure 3).[18] The isosbestic points were not clear because of a smaller amount of change in the absorption and the smaller absorption ratio attributed to DPA compared to that of PPV. A similar complexation behavior between **DPA-PPV G1** (**2a**−**4a**) and $SnCl_2$ was also confirmed.

In conclusion, we have synthesized novel poly(*p*-phenylenevinylene)s (PPVs) with dendritic phenylazomethines (DPA) obtained via the Heck reaction by complexing monomers with metal ions in advance, providing a new metal-collecting conjugated polymer.

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Supporting Information Available: Detailed experimental procedures of palladium-catalyzed reactions and characterization data of **DPA-Br$_2$ G*n***, **DPA-DSB G*n***, **1**, and **DPA-PPV**s. This material is available free of charge via the Internet at http://pubs.acs.org.

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[17] Excited at their absorption maximum.

[18] We at least identified the number of metal ions by UV−vis spectroscopy. On the basis of the result, Sn^{2+} ions bind to all the binding sites. The number agreed with the imine units determined by the hydrolysis method.