

ORIGINAL ARTICLE

Construction of multi-*N*-heterocycle-containing organic solvent-soluble polymers with 1,3,4,6,9b-pentaazaphenylene

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Multi-*N*-heterocycles could be a useful platform for constructing network structures via hydrogen bonds and for realizing catalyzed organic reactions. In addition, unique optical properties can be achieved by their incorporation into polymers. In this manuscript, the synthesis and characterization of an organic solvent-soluble polymer containing 1,3,4,6,9b-pentaazaphenylene are presented. From a series of optical measurements and comparative studies with model compounds, we investigated the electronic structures of polymer main chains containing the azaphenylene unit.

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Keywords: azaphenylene; *N*-heterocycles; π -conjugation

INTRODUCTION

Multi-*N*-heterocycles are versatile nanobuilding blocks for the construction of nanostructures and also for molecular recognition. By the formation of complexes via hydrogen or dative bonds with the nitrogen atoms, unique structures can be fabricated from these materials. In addition, the precise molecular recognition based on complexation has been accomplished with various targets involving biomolecules.^{1–4} Furthermore, recent works have revealed the useful photo-catalytic activity of carbon nitrides, which possess network structures composed of three-fused multi-*N*-heterocycles.⁵ Notably, the decomposition of water with visible light irradiation has been achieved with carbon nitrides, without requiring the use of rare metals. Despite the utility of multi-*N*-heterocycles, the poor solubility of these compounds often occludes the analysis of their molecular structure and reaction mechanisms. Consequently, the applicability of the materials is critically limited. Improving the solubility and processability of these materials is essential to advance the fundamental chemistry and explore the applications of multi-*N*-heterocycles.

Azaphenalenenes are a class of fused three-ring compounds in which the carbon at the center is replaced by nitrogen (Scheme 1).^{6–23} Compared with phenalene, it was previously shown that azaphenylene has higher stability, even in the neutral state, because the unpaired electrons of the center nitrogen participate can be conjugated to form 14π electronic systems. Indeed, from the first synthesis of 9b-azaphenylene in 1976,⁷ the series of azaphenalenenes have been isolated in a neutral form.^{6–17} Moreover, their optical properties and electronic structures have been examined.⁷ However, to the best of our knowledge, few studies on the conjugation of azaphenalenenes

and other functional molecules have been executed. In particular, the influence of conjugation on the electronic structures of azaphenalenenes has hardly been examined. Thus, the introduction of azaphenalenenes into polymers and the investigation of their material properties are of great significance for the development of new functional materials, including those with interesting optical properties derived from the electronic structure of azaphenalenenes.

Herein, we report the synthesis and optical properties of an organic solvent-soluble polymer incorporating the dimethyl-1,3,4,6,9b-pentaazaphenylene (**5AP**) unit. Initially, dibromo-substituted **5AP** was prepared as a monomer. An alternating polymer with fluorene was obtained by Suzuki–Miyaura coupling reactions. The optical properties of the synthesized polymer were measured to understand the electronic structures of the polymer. Accordingly, from comparative studies with the model compounds, electronic interactions between **5AP** and fluorene units were observed. Delocalization of the highest occupied molecular orbital (HOMO) through the **5AP** unit was suggested from computer modeling of the frontier orbitals of the **5AP**-containing polymer main chain.

EXPERIMENTAL PROCEDURE

General

¹H nuclear magnetic resonance (NMR) and ¹³C NMR spectra were measured with a JEOL EX-400 (400 MHz for ¹H and 100 MHz for ¹³C) spectrometer (JEOL Ltd., Tokyo, Japan). Coupling constants (*J* value) are reported in Hertz. ¹H and ¹³C NMR spectra used tetramethylsilane as an internal standard. The number-average molecular weight (M_n) and the molecular weight distribution (weight-average molecular weight/number-average molecular weight (M_w/M_n)) values of all polymers were estimated by size-exclusion

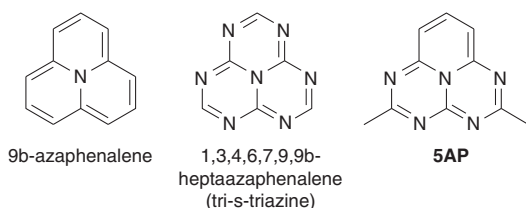
chromatography, performed on a TOSOH G3000HXI (TOSOH Co., Ltd., Tokyo, Japan) system equipped with three consecutive polystyrene gel columns (TOSOH gels: α -4000, α -3000 and α -2500) and an ultraviolet detector at 40 °C. The system was operated at a flow rate of 1.0 ml min⁻¹ with CHCl₃ as an eluent. The system was calibrated with polystyrene standards. Ultraviolet-visible spectra were recorded on a Shimadzu UV-3600 spectrophotometer (Shimadzu Co., Ltd., Kyoto, Japan). Fluorescence emission spectra were recorded on a HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer (HORIBA Ltd., Kyoto, Japan), and the absolute quantum yield was calculated with the integrating sphere on the HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer in chloroform. Cyclic voltammetry spectra were recorded on a BAS ALS electrochemical analyzer model 600D (BAS Inc., Tokyo, Japan). Molecular orbital calculations were performed using Gaussian 09 software package.

5AP

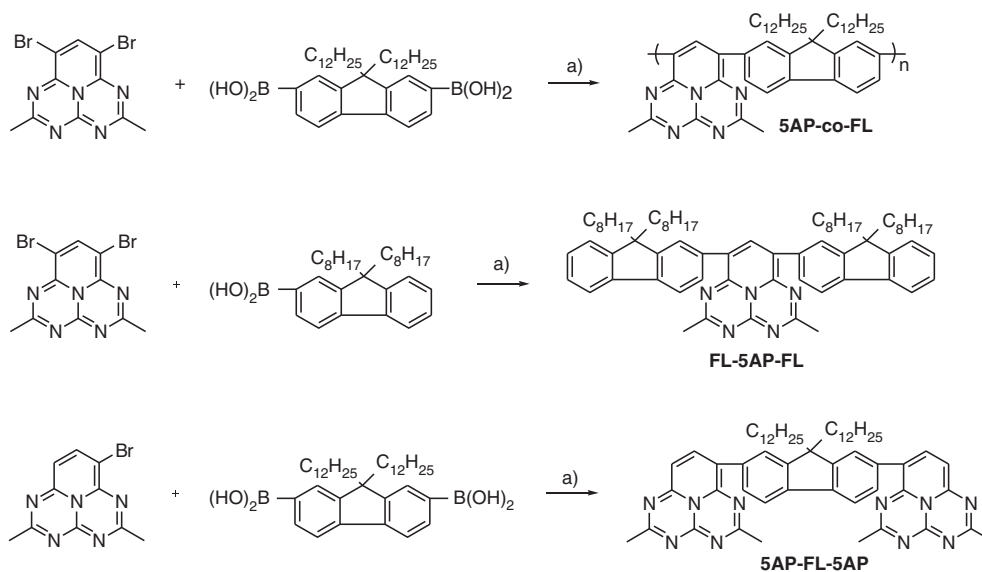
A glyme solution (10 ml) containing 2,6-diaminopyridine (8.73 g, 80.0 mmol) and methyl-*N*-cyanoacetimidate (15.67 g, 160.0 mmol) was refluxed overnight, after which volatiles were removed under vacuum.¹⁵ The residual solid was recrystallized twice from methanol and chloroform to obtain the product (6.02 g, 30.2 mmol, 38%) as a red crystal. ¹H NMR (CDCl₃, p.p.m.) 7.27 (t, *J* = 8.3 Hz, 1H), 6.09 (d, *J* = 8.3 Hz, 2H), 2.03 (s, 6H). ¹³C NMR (CDCl₃, p.p.m.) 177.66, 159.53, 154.23, 145.74, 110.73, 25.60. High resolution mass spectrometry (positive mode, electron spray ionization) HRMS (p-ESI) calcd. for C₁₀H₉N₅ + H⁺: *m/z* = 200.0931; found: *m/z* = 200.0928.

7,9-Dibromo-2,5-dimethyl-1,3,4,6,9b-pentaazaphenalene

A chloroform solution (250 ml) of 5AP (4.00 g, 20.1 mmol) and *N*-bromosuccinimide (10.7 g, 60.3 mmol) was refluxed for 3 days. The residual solution



Scheme 1 Chemical structures of phenalene derivatives. 5AP, dimethyl-1,3,4,6,9b-pentaazaphenalene.



^aReagents and conditions: a) Pd₂(dba)₃, S-Phos, Cs₂CO₃, toluene, H₂O, 85 °C, 3 d.

Scheme 2 Synthesis of the polymer and model compounds. ^aReagents and conditions: (a) Pd₂(dba)₃, S-Phos, Cs₂CO₃, toluene, H₂O, 85 °C, 3 days.

was evaporated under vacuum. After flash chromatography on silica gel (9:1 CHCl₃/EtOAc, R_f = 0.3), followed by recrystallization from ethanol, the product (3.82 g, 10.7 mmol, 53%) was obtained as a purple powder. ¹H NMR (CDCl₃, p.p.m.) 7.85 (s, 1H), 2.14 (s, 6H). ¹³C NMR (CDCl₃, p.p.m.) 179.15, 150.93, 150.67, 102.49, 26.06. HRMS (p-ESI) calcd. for C₁₀H₇Br₂N₅ + H⁺: *m/z* = 355.9141; found: *m/z* = 355.9137.

7-Bromo-2,5-dimethyl-1,3,4,6,9b-pentaazaphenalene

A chloroform solution (10 ml) of 5AP (200 mg, 1.0 mmol) and *N*-bromosuccinimide (178 mg, 1.0 mmol) was refluxed for 2 h. The residual solution was evaporated under vacuum. The product (202 mg, 0.73 mmol, 73%) was obtained as a purple powder after recrystallization from ethanol. ¹H NMR (CDCl₃, p.p.m.) 7.54 (d, *J* = 8.8 Hz, 1H), 6.03 (d, *J* = 8.9 Hz, 1H), 2.12 (s, 3H), 2.05 (s, 3H). ¹³C NMR (CDCl₃, p.p.m.) 179.19, 177.84, 159.61, 153.65, 151.51, 148.56, 110.70, 103.03, 26.07, 25.69. HRMS (p-ESI) calcd. for C₁₀H₉BrN₅ + H⁺: *m/z* = 278.0036; found: *m/z* = 278.0033.

Fluorene (FL)-5AP-FL

A solution containing tris(dibenzylideneacetone)dipalladium(0) (Pd₂(dba)₃; 1 mg, 0.001 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-Phos; 3 mg, 0.007 mmol), cesium carbonate (Cs₂CO₃; 0.40 g, 1.23 mmol), 7,9-dibromo-2,5-dimethyl-1,3,4,6,9b-pentaazaphenalene (35.7 mg, 0.10 mmol) and 9,9-didodecylfluorene-2-boronic acid (87 mg, 0.20 mmol) in 1 ml of toluene and 1 ml of H₂O was stirred at 85 °C for 2 days under an argon atmosphere. The product was precipitated by adding 50 ml of methanol and then washing with methanol twice to obtain a dark blue solid (60 mg, 61%). ¹H NMR (CDCl₃, p.p.m.) 7.73–7.67 (m, 5H), 7.60 (s, 2H), 7.39 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.37–7.29 (m, 6H), 2.00 (s, 6H), 1.96 (t, *J* = 8.3 Hz, 8H), 1.18 (m, 8H), 1.05 (m, 32H), 0.81 (t, *J* = 7.0 Hz, 12H), 0.70 (m, 8H). ¹³C NMR (CDCl₃, p.p.m.) 177.00, 151.19, 151.08, 150.20, 146.30, 141.25, 140.45, 133.16, 127.30, 126.89, 126.80, 123.46, 123.13, 122.94, 119.83, 119.46, 55.02, 40.27, 31.75, 30.16, 29.26, 25.76, 23.89, 22.56, 14.04. HRMS (p-ESI) calcd. for C₆₈H₈₉N₅ + H⁺: *m/z* = 976.7191; found: *m/z* = 976.7177.

5AP-FL-5AP

A solution containing Pd₂(dba)₃ (1 mg, 0.001 mmol), S-Phos (3 mg, 0.007 mmol), Cs₂CO₃ (0.40 g, 1.23 mmol), 7-bromo-2,5-dimethyl-1,3,4,6,9b-pentaazaphenalene (56 mg, 0.20 mmol) and 9,9-didodecylfluorene-2,7-diboronic acid (59 mg, 0.10 mmol) in 1 ml of toluene and 1 ml of H₂O was stirred at

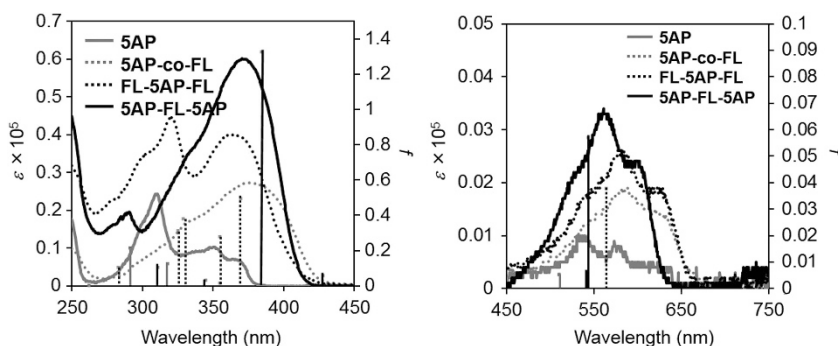


Figure 1 Ultraviolet–visible spectra of the dimethyl-1,3,4,6,9b-pentaazaphenylene (**5AP**) derivatives in CHCl_3 ($1.0 \times 10^{-5} \text{ M}$) and time-dependent density functional theory calculated (B3LYP/6–31G + d) oscillator strengths (color bar). ϵ = molar extinction coefficient and f = oscillator strength.

85°C for 2 days under an argon atmosphere. After the reaction was refluxed for 2 days, the resulting mixture was poured into brine, extracted with cyclopentyl methyl ether and dried with anhydrous Na_2SO_4 . After the solvent was removed, the crude product was purified by silica gel column chromatography with an ethyl acetate/chloroform (1:1) eluent to afford the product (60 mg, 67%). ^1H NMR (CDCl_3 , p.p.m.) 7.68 (d, $J = 7.9$ Hz, 2H), 7.50 (s, 2H), 7.47 (d, $J = 8.5$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 6.21 (d, $J = 8.5$ Hz, 2H), 2.04 (s, 6H), 1.99 (s, 6H), 1.92 (m, 4H), 1.31–0.98 (m, 36H), 0.86 (t, $J = 6.8$ Hz, 6H), 0.72 (br, 4H). ^{13}C NMR (CDCl_3 , p.p.m.) 177.45, 177.38, 160.36, 153.33, 151.95, 150.66, 146.09, 141.65, 140.49, 133.30, 126.90, 123.24, 119.60, 110.59, 103.35, 99.55, 54.98, 40.14, 31.85, 30.22, 29.64, 29.56, 29.50, 29.27, 26.77, 26.64, 25.89, 25.56, 23.97, 22.62, 14.07. HRMS (p-ESI) calcd. for $\text{C}_{57}\text{H}_{72}\text{N}_{10}^+$ H^+ : $m/z = 897.5993$; found: $m/z = 897.6014$.

5AP-co-FL

A solution containing $\text{Pd}_2(\text{dba})_3$ (2 mg, 0.002 mmol), S-Phos (6 mg, 0.015 mmol), Cs_2CO_3 (0.80 g, 2.46 mmol), 7,9-dibromo-2,5-dimethyl-1,3,4,6,9b-pentaazaphenylene (68 mg, 0.19 mmol) and 9,9-didodecylfluorene-2,7-diboronic acid (112 mg, 0.19 mmol) in 1 ml of toluene and 1 ml of H_2O was stirred at 85°C for 3 days under an argon atmosphere. The product was obtained as a deep blue solid (110 mg, 83%) after adding 50 ml of methanol to precipitate the compound and then washing twice with methanol. ^1H NMR (CDCl_3 , p.p.m.) 7.72 (1H), 7.69 (2H), 7.62 (2H), 7.36 (2H), 2.01 (10H), 1.20 (40H), 0.86 (6H). ^{13}C NMR (CDCl_3 , p.p.m.) 117.11, 161.07, 151.16, 150.75, 150.25, 146.31, 140.60, 133.52, 133.12, 127.35, 127.05, 123.63, 123.50, 123.24, 123.01, 119.85, 119.72, 119.48, 55.09, 40.30, 40.23, 31.92, 30.38, 30.20, 29.76, 29.63, 29.58, 29.44, 29.34, 25.79, 24.15, 23.94, 22.68, 14.12. Anal. Calcd. for $\text{C}_{49}\text{H}_{68}\text{N}_5$: H, 9.80; C, 80.61; N, 9.5. Found: H, 7.95; C, 66.29; N, 5.91.

RESULTS AND DISCUSSION

We designed a monomer based on the tri-*s*-triazine skeleton because of its relatively high stability in the series of azaphenolens.^{15,16} The two carbons at the α -position (C8 and C9) of tri-*s*-triazine were replaced with nitrogen. The C4 and C5 positions of the monomer were substituted with methyl groups to improve stability and enhance reactivity. To prepare the monomer, **5AP** was halogenated at the α -carbons (C8 and C9) for the coupling reaction.¹⁷ From X-ray crystal structure analysis, it was found that the sum of the bond angle around N1 was approximately 360° .^{24–27} These data indicated that **5AP** was a highly planar molecule. Such planarity is favorable to realize the delocalization of electrons in aromatic compounds. In addition, the unpaired electrons of N1 were delocalized in the cyclic system of **5AP**.²⁷ These data indicate that a 14π electronic conjugation system, including the unpaired electrons at the N1 position, was obtained.

Polymerization of the dibromo-substituted **5AP**¹⁷ with fluorenyldiboronic acid via Suzuki–Miyaura coupling was performed

Table 1 Optical properties of the **5AP** derivatives

Compounds	$\lambda_{\text{abs,max}}$ (nm) ^a	$\lambda_{\text{em,max}}$ (nm) ^b	Φ_{PL}^c
5AP	309, 350, 533	391	0.006
5AP-co-FL	376, 584	420	0.008
FL-5AP-FL	320, 363, 578	385	0.010
5AP-FL-5AP	372, 561	417	0.004

Abbreviation: **5AP**, dimethyl-1,3,4,6,9b-pentaazaphenylene.

^aMeasured in CHCl_3 ($1.0 \times 10^{-5} \text{ M}$) at room temperature.

^bExcited at absorption maxima.

^cDetermined as an absolute value in chloroform.

(Scheme 2). After re-precipitation from methanol to remove the metal species and small molecules derived from the monomers, the polymeric products were obtained. A series of measurements were performed to characterize the products. The number-average molecular weight (M_n) of the polymer determined from gel permeation chromatography analysis was 3600 (degree of polymerization = 5), and the polydispersity index was 1.45. The polymer showed good solubility in conventional organic solvents such as chloroform, dichloromethane and tetrahydrofuran. The introduction of nitrogen was confirmed by elemental analysis, suggesting that the product had the expected structure. By increasing the reaction time (4 days), a larger molecular weight polymeric product was obtained ($M_n = 10\,600$, polydispersity index = 1.69, degree of polymerization = 14), whereas the solubility was only slightly reduced. Because the degree of polymerization in the shorter polymer was greater than five, the two polymer products could be used to evaluate the effect of extending the polymer main chain on the optical properties. Two model compounds, **FL-5AP-FL** and **5AP-FL-5AP**, were also synthesized by Suzuki–Miyaura coupling. From the ^1H and ^{13}C NMR spectra, similar signal patterns involving **5AP** and the fluorene units on the polymer and the model compounds were obtained. Thus, we concluded that the polymer and the model compounds possessed the designed chemical structures, including **5AP**, and were of sufficient purity for the evaluation of optical properties.

The electronic structures of the synthesized **5AP** derivatives at the ground states were investigated by ultraviolet–visible absorption measurements. Figure 1 shows the spectra of chloroform solutions ($1.0 \times 10^{-5} \text{ M}$, repeat unit reference). The optical properties are summarized in Table 1. **5AP** presented absorption bands with peaks from 260 to 370 nm (π – π^*) as well as very weak absorption bands from 500 to 600 nm (lone pair orbital at the nitrogen center– π^*). The model compounds **5AP-FL-5AP** and **FL-5AP-FL** showed absorption bands with peaks at approximately 370 nm (π – π^*) of the fluorene

unit) and approximately 580 nm (lone pair orbital- π^* of the **5AP** unit). Interestingly, **5AP-co-FL** exhibited significantly redshifted absorption bands compared with those of **5AP** and the model compounds. In particular, a shift of the absorption band at approximately 370 nm of **5AP-co-FL**, assigned as the π - π^* transition in the fluorene unit, was observed compared with that of **5AP-FL-5AP**. The optical properties of meta-substituted diphenylacetylene were previously examined with a dendritic system.^{28–30} A peak shift was hardly observed by extending the chain length. Thus, comparing to that work, these results obtained here for the polymer suggest that electronic interactions can occur through the polymer main chain involving the **5AP** unit. The HOMO levels of **5AP** derivatives can be perturbed by the inductive effect.¹⁰ Substituent effects could also be responsible for the peak shift of the absorption band at approximately 580 nm. The absorption spectrum of the longer polymer was measured, and less significant changes were observed (Supplementary Figure 1). Thus, the results suggest that electronic interactions can occur within five repeating units.

The emission properties of the **5AP** derivatives were examined in CHCl_3 (Figure 2). According to a previous report,¹⁰ it is known that the S_0 - S_1 transition of **5AP** is attributed to a lone pair orbital- π^* transition. When excited with light at the peak wavelength of the strong absorption band in the ultraviolet region (π - π^*), which was

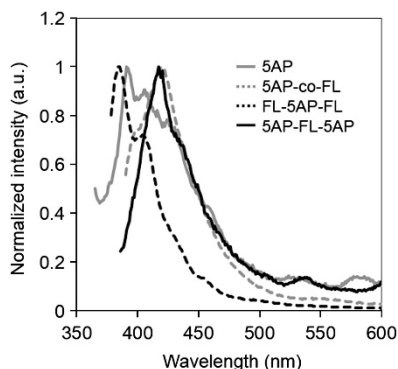


Figure 2 Normalized photoluminescence spectra of dimethyl-1,3,4,6,9b-pentaazaphenalene (**5AP**) derivatives in CHCl_3 ($1.0 \times 10^{-5} \text{ M}$). (Excited at absorption maxima, respectively).

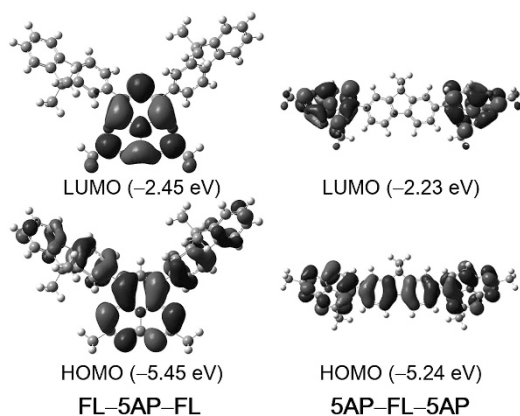


Figure 3 Molecular orbital diagrams for the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of **FL-5AP-FL** and **5AP-FL-5AP** (B3LYP/6-31G++(d)). **5AP**, dimethyl-1,3,4,6,9b-pentaazaphenalene.

attributed to the S_0 - S_2 transition, **5AP** derivatives showed weak emission. Although the quantum yields of these emissions were low ($\Phi_{\text{PL}} \leq 0.01$), the emission properties represent the electronic interactions at the excited states. **5AP** also presented weak emission, with the peaks at approximately 390 nm. Importantly, the emission bands obtained from **5AP-co-FL** and **5AP-FL-5AP** were at longer wavelengths compared with **5AP**. These results suggest the existence of electronic interactions involving the **5AP** units in the excited states. The energy level of the non-bonding electrons of the nitrogen in **5AP** is higher than the HOMO of fluorene. Therefore, photo-induced electron transfer can occur in the excited states, and **5AP** works as a quencher in the polymers.

To further understand the nature of **5AP** and the electronic structures, we performed theoretical calculations for **5AP**, **FL-5AP-FL** and **5AP-FL-5AP** using the density functional theory method at the B3LYP/6-31G++(d) level.³¹ The long alkyl chains were replaced with methyl groups simplify the calculation. Figure 3 illustrates the diagrams of each HOMO and lowest unoccupied molecular orbital

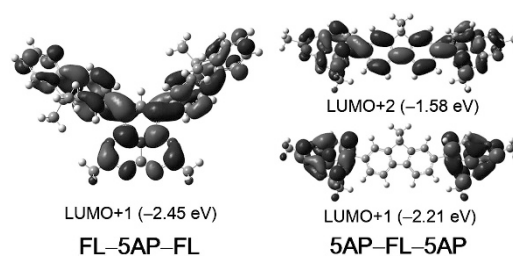


Figure 4 Molecular orbital diagrams for the lowest unoccupied molecular orbital (LUMO)+1 and LUMO+2 of **FL-5AP-FL** and **5AP-FL-5AP** (B3LYP/6-31G++(d)). **5AP**, dimethyl-1,3,4,6,9b-pentaazaphenalene.

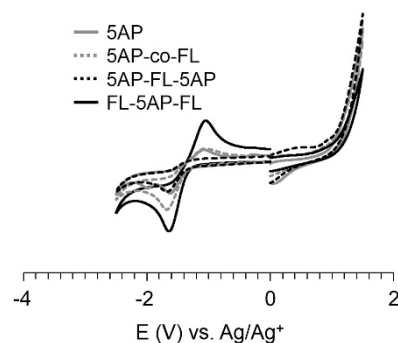


Figure 5 Cyclic voltammograms (electrolyte solution: $0.1 \text{ M Bu}_4\text{NPF}_6$ in tetrahydrofuran; scan rate: 0.1 V s^{-1} ; reference electrode: Ag/Ag^+).

Table 2 Electronic energy levels of the **5AP** derivatives

Compounds	E_{HOMO} (eV) ^a	E_{LUMO} (eV) ^a	E_{gap} (eV) ^a	E_{gap} (eV) ^b
5AP	-5.77	-3.21	2.56	3.29
5AP-co-FL	-5.62	-3.24	2.38	2.94
FL-5AP-FL	-5.69	-3.22	2.47	2.98
5AP-FL-5AP	-5.70	-3.23	2.47	3.01

Abbreviations: **5AP**, dimethyl-1,3,4,6,9b-pentaazaphenalene; HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital.

^aDetermined from cyclic voltammograms in Figure 5. HOMO (or LUMO) (eV) = $-4.8 - (E_{\text{onset}} - E_{1/2(\text{Ferrocene})})$.

^bCalculated by absorption onsets around 400 nm.

(LUMO) of **FL-5AP-FL** and **5AP-FL-5AP**. In agreement with the results of the optical measurements, HOMOs were expanded through the **5AP** and fluorene moieties. It is assumed that these delocalized HOMOs could be responsible for the redshifts of the absorption and the emission bands.

The electronic oscillator strength (f) was calculated using the time-dependent density functional theory method at the B3LYP/6-31G + (d) level (Figure 1).³¹ The calculated energy levels of each orbital showed good agreement with the experimental values. The absorption bands were assigned according to the calculation results. The bands between 500 and 600 nm should correspond to the HOMO → LUMO transition from the main chain to the **5AP** moiety. The π – π^* transition of the main chain observed at 384 nm in **5AP-FL-5AP** was assigned to the HOMO → LUMO + 2 transition, and the band at 364 nm in **FL-5AP-FL** was assigned to the HOMO → LUMO + 1 transition (Figure 4).

The energy gaps between the HOMO and LUMO levels were estimated using the data from the cyclic voltammetry and optical measurements (Figure 5 and Table 2). In the cyclic voltammetry measurements, the energy gaps were calculated from the peak positions. From the absorption measurements, the desired values were evaluated from the onset of the absorption bands, with the peak at approximately 400 nm assigned to the π – π^* transition from the HOMO to LUMO + 1 or + 2, rather than assigning the small absorption bands at approximately 550 nm to the HOMO – LUMO gaps. The results showed that the energy gaps of the models calculated by both methods were smaller than that of **5AP**. Furthermore, the polymer presented the narrowest energy gap of the **5AP** derivatives, as reported in a previous study.¹⁰ These data also support the existence of electronic interactions through the polymer main chains involving **5AP**.

CONCLUSIONS

We synthesized an organic solvent-soluble polymer composed of the **5AP** unit. From the series of optical measurements and computational calculations, electronic interactions between **5AP** and the fluorene co-monomer were suggested. These results imply that the optical properties of **5AP** units can be tuned via electronic coupling with the co-monomers through the polymer main chains. Furthermore, because of the structural similarity of azaphenylene to the monomer unit of carbon nitride, we expect that the **5AP**-containing polymers might be useful as a soluble analog to carbon nitride. Studies on the photo-catalytic ability of **5AP**-containing polymers are in progress.

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