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Highlight Review

π-Electron-system-layered Polymers Based on [2.2]Paracyclophane

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Abstract

Incorporation of a [2.2]paracyclophane skeleton into a conjugated polymer main chain affords a polymer comprising stacked π-electron systems. In this article, we describe the synthesis and optical properties of some [2.2]paracyclophane-based polymers on the basis of the results of our resent research. We discuss the role of [2.2]paracyclophane in the polymer backbone, through-space conjugation of the polymer, and the feasibility of using the titled polymers as single molecular wires that allow for unidirectional energy and charge transfer via through-space interactions.

◆ Introduction

"Cyclophanes" constitute a class of compounds comprising a hydrocarbon with an aromatic unit and an aliphatic chain bridging two nonadjacent positions of the aromatic ring.[1] A typical example of this class is [2.2]paracyclophane, which is the main focus of this study. Various other cyclic compounds such as calixarenes and annulenes have also been classified as cyclophanes. The first synthesis of [2.2]paracyclophane by the pyrolysis of *p*-xylene was reported by Brown and Farthing in 1949.[2] Following Cram and Steinberg's report on a practical synthetic route to [2.2]paracyclophane, i.e., the Wurtz type intramolecular cyclization of 1,4-bis(bromomethyl)benzene,[3] several methods for [2.2]paracyclophane synthesis have been developed,[1] thus making this compound commercially available.

The reactivities, optoelectronic properties, and theoretical studies of [2.2]paracyclophane and its derivatives have been widely investigated in the field of organic chemistry.[1] Recently, examples of cyclophane-containing polymers were comprehensively reviewed.[4] Despite the large number of intensive studies on cyclophane chemistry in the last five decades, conjugated polymers containing cyclophane skeletons in the main chain were largely ignored until our first report in 2002.[5] The reported cyclophane-containing polymers are insoluble in common organic solvents and do not have film-forming ability; hence, their structures and properties have not been elucidated in detail.[6,7a]

We have focused on the structure of [2.2]paracyclophane and studied on the synthesis and properties of conjugated polymers containing [2.2]paracyclophane in the main chains as a repeating unit by the polymerization of [2.2]paracyclophane monomers with various aromatic compounds as comonomers. Incorporation of the [2.2]paracyclophane skeleton into the conjugated polymer backbone results in a partly π-stacked and layered structure of π-electron systems. This article presents a brief summary of the synthesis and fundamental properties (e.g., through-space conjugation and emission behaviors) of π-electron-system-layered polymers based on [2.2]paracyclophane.

◆ Synthesis of π-Electron-system-layered Polymers Based on [2.2]Paracyclophane

Palladium-catalyzed cross-couplings can be used for the synthesis of various π-conjugated molecules and polymers through sp^2 and sp carbon–carbon bond formation.[8] We have prepared poly(*p*-aryleneethynylene) (PAE)-type cyclophane-containing polymers[9] by the Sonogashira–Hagihara coupling.[10] Polymerization of pseudo-*p*-diethynyl[2.2]paracyclophane[9b] (**1**) with diiodobenzene comonomer **2** (Scheme 1) proceeded smoothly in the presence of a catalytic amount of $[Pd(PPh_3)_4]$ and CuI to afford polymer **3** in 95% isolated yield with number-average molecular weight (M_n) of 14500 and polydispersity index (PDI) of 2.4. Pseudo-*o*-diethynyl[2.2]paracyclophane[11] (**4**) could be polymerized with **2** in the presence of the same catalytic system to obtain the corresponding zigzag polymer **5** in 23% isolated yield ($M_n = 3800$, $PDI = 1.3$), as shown in Scheme 1.[9g] The reactivity of **4** toward the Sonogashira–Hagihara protocol was relatively poor because of steric hindrance around the ethynyl groups of pseudo-*o*-disubstituted [2.2]paracyclophane during polymerization, which explained the low yield and M_n of the product.

Poly(*p*-arylenevinylene) (PAV)-type cyclophane polymers[12] have been prepared by the Mizoroki–Heck cross-coupling.[13] For example, the $Pd(OAc)_2/P(o\text{-}Tol)_3$-catalyzed reaction of pseudo-*p*-divinyl[2.2]paracyclophane[12a,14] (**6**) with diiodofluorene monomer **7** afforded the corresponding polymer **8** in 96% isolated yield with M_n and PDI of 5200 and 2.1,[12b] respectively, as shown in Scheme 2.

In addition to transition-metal-catalyzed cross-coupling, there are some more useful reactions for the synthesis of PAV-type polymers. The Knoevenagel reaction can be adopted to synthesize PAVs with an electron-withdrawing substituent at the olefin moiety.[15] As shown in Scheme 3, we applied this reaction to prepare π-electron-system-layered polymers based on [2.2]paracyclophane. The treatment of pseudo-*p*-diformyl[2.2]-

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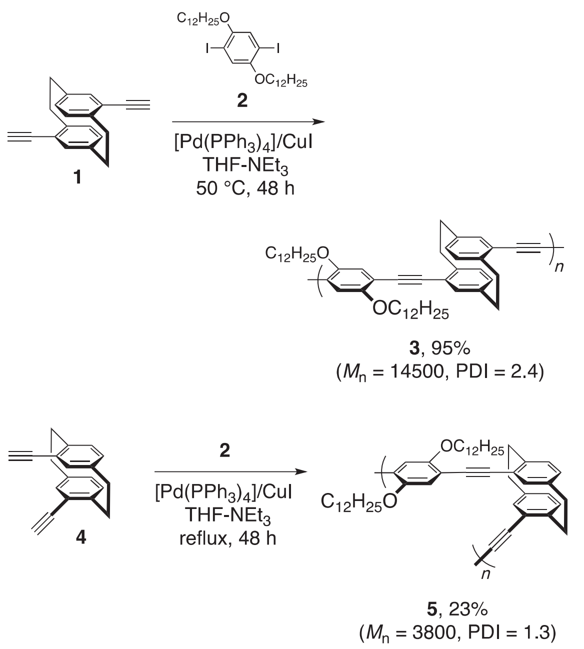
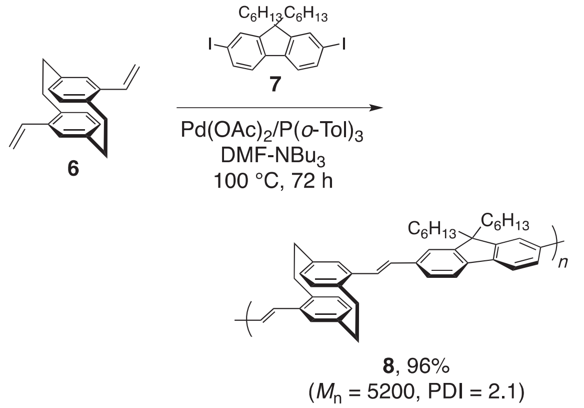


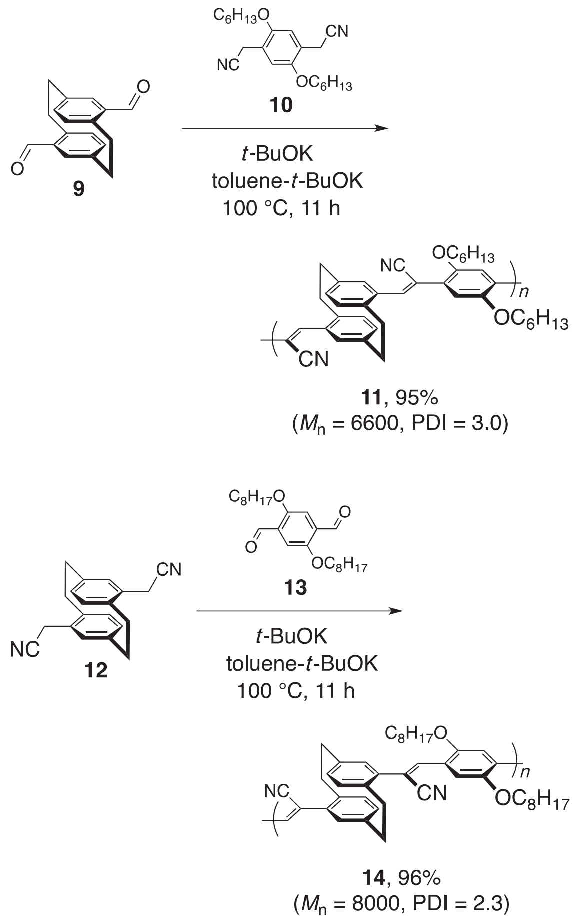
Scheme 1. Synthesis of PAE type π-electron-system-layered polymers by Sonogashira–Hagihara coupling.



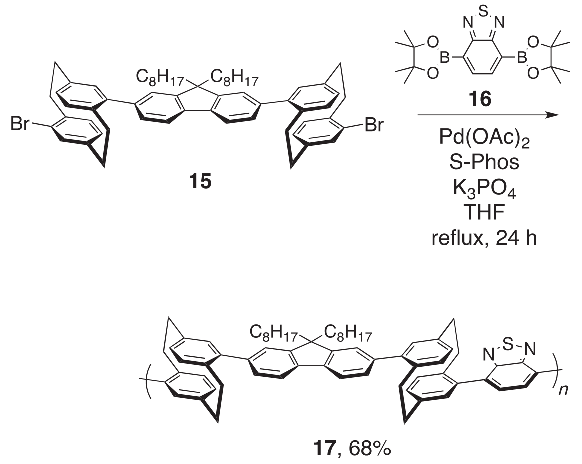
Scheme 2. Synthesis of PAV type π-electron-system-layered polymer by Mizoroki–Heck coupling.

paracyclophane (**9**) with bis(cyanomethyl)benzene monomer **10** in the presence of *t*-BuOK gave cyano-substituted PAV **11** in 95% isolated yield ($M_n = 6600$, PDI = 3.0).[16] PAV **14**, which also had cyano substituents but at positions different from those in PAV **11**, was obtained in 96% isolated yield ($M_n = 8000$, PDI = 2.3) by the Knoevenagel reaction of pseudo-*p*-bis(cyanomethyl)[2.2]paracyclophane (**12**) and diformylbenzene monomer **13** (Scheme 3).

A representative example of the synthesis of cyclophane-containing poly(*p*-arylene) (PA)-type polymers[17] by the Suzuki–Miyaura cross-coupling is shown in Scheme 4.[18] The reaction of [2.2]paracyclophane-containing monomer **15** with bis(boronic acid pinacol ester) monomer **16** in the presence of a $Pd(OAc)_2$/S-Phos (= 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl) catalytic system[19] afforded the donor–acceptor-type PA **17** in 68% isolated yield ($M_n = 17000$, PDI = 2.9) (Scheme 4).[17b]



Scheme 3. Synthesis of PAV type π-electron-system-layered polymers by Knoevenagel reaction.



Scheme 4. Synthesis of PA type π-electron-system-layered polymer by Suzuki–Miyaura coupling.

Oxidative coupling reaction of electron-rich aromatic rings was also employed for obtaining cyclophane-containing PAs; namely, oligothiophene-substituted [2.2]paracyclophanes were polymerized by iron-catalyzed oxidation and electrochemical oxidation polymerization.[7]

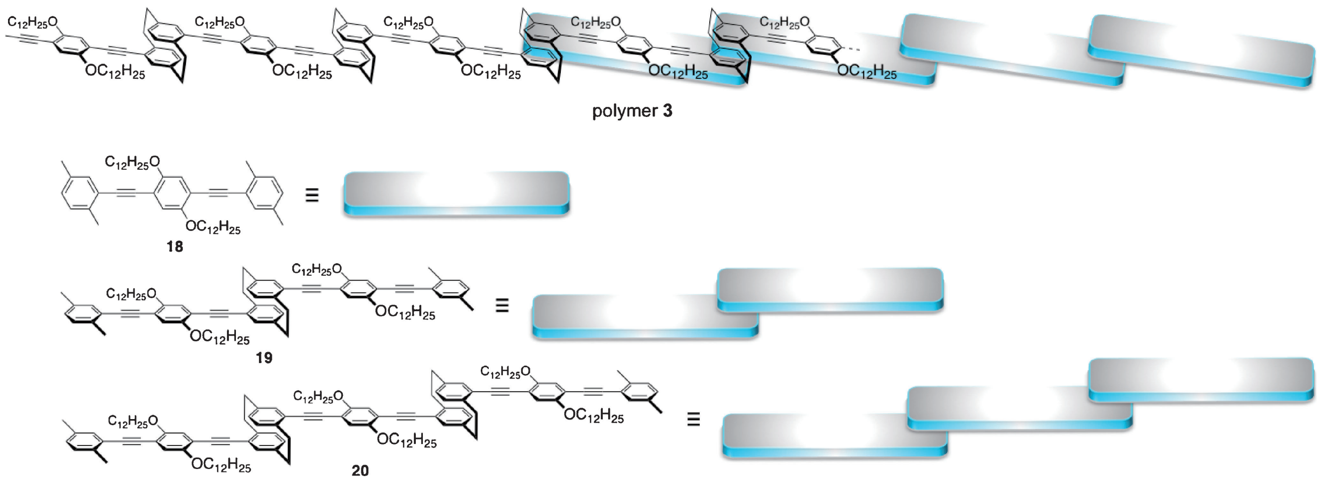


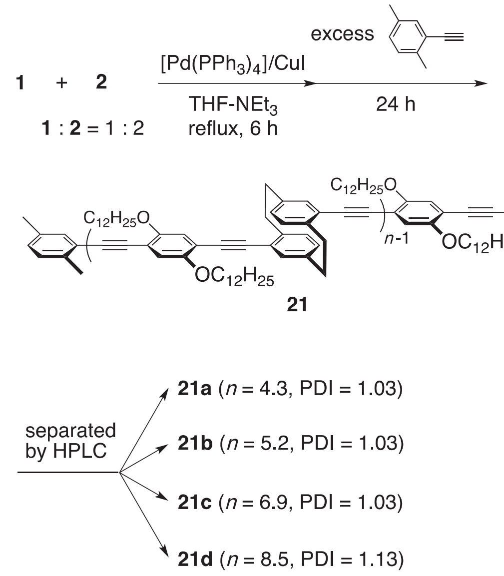
Figure 1. π-Electron-system-layered structures of polymer **3** and compounds **18**–**20**.

All the aforementioned polymers had long alkyl side chains, because of which they were soluble in common organic solvents such as THF, toluene, $CHCl_3$, and CH_2Cl_2. Therefore, accurate structure elucidation by ^1H and ^{13}C NMR spectroscopy in $CDCl_3$ or CD_2Cl_2 solutions was possible. In addition, owing to their excellent film-forming ability, spin-coated thin films of these polymers were readily obtained from toluene solutions.

Through-space Conjugation of π-Electron-system-layered Polymers

This section discusses the structure of [2.2]paracyclophane-containing polymers. In the case of cyclophane-containing polymers, the so-called π-conjugation is broken by the space between two benzene rings of the [2.2]paracyclophane unit. PAE **3** is illustrated in Figure 1 as a representative example; this polymer has a unique structure, in which the π-electron systems of compound **18** are partly stacked and layered one-dimensionally. The [2.2]paracyclophane units act as bridges linking the π-electron systems to form new arylene–ethynylene (AE) π-electron systems, i.e., xylenyl–ethynylene–phenylene–ethynylene–xylenyl units resembling the structure of **18**. Thus, since the leading part of PAE **3** is not [2.2]paracyclophane but the PA π-electron system, the optical and electrochemical properties of this polymer depend only on those of **18** regardless of [2.2]paracyclophane.

To study the conjugation system of the polymers in further detail, compounds **19** and **20** with two and three layers of PA π-electron systems, respectively, were prepared.[20] In addition, end-capped PAE **21** was synthesized and separated into four fractions **21a**–**21d** using HPLC, as shown in Scheme 5. Figure 2A shows the UV–vis absorption spectra of compounds **18**–**20**, polymers **21a**–**21d**, and **3** in diluted $CHCl_3$ solutions (1.0×10^{-5} M). All the compounds and polymers exhibited a typical π–π^* transition band attributable to the AE skeleton. The absorption maxima (λ_{max}) of **18**–**20** were observed at 371, 378, and 381 nm, respectively; λ_{max} and absorption edges exhibited a bathochromic shift with an increase in the number of layered PA π-electron systems. Such a bathochromic shift was also observed in the λ_{max} values and absorption edges of polymers **21a**–**21d** with an increase in M_n; among these, λ_{max} of **21d** appeared at 386 nm.



Scheme 5. Synthesis and separation of π-electron-system-layered polymers **21a**–**21d**.

A linear relationship exists between the band gap energy (E_g/cm^{-1}) estimated from λ_{max} and the reciprocal of the number of repeating units ($1/n$) in a conjugated polymer. We investigated whether this relationship holds good for π-electron-system-layered polymers comprising the through-space interactions. The plot of E_g against $1/n$ for compounds **18**–**20** and polymers **21a**–**21d** (Figure 2B) was reflective of a linear relationship ($R^2 = 0.99$), indicating the existence of through-space conjugation. On the basis of this relationship, λ_{max} of the polymers ($n = \infty$) was predicted to be 388 nm, which was in good agreement with the observed λ_{max} (387 nm) of PAE **3** ($M_n = 14500$, $n = 21$, PDI $= 2.4$). According to the empirical power–law relationship ($E = 1/\lambda_{max} \sim n^{-x}$) and the data pertaining to compounds **18**–**20** and polymers **21a**–**21d**, the effective through-space conjugation repeating unit number (n) was estimated to be 11.4. On the other hand, Nakano and co-workers reported that the electronic interactions among the

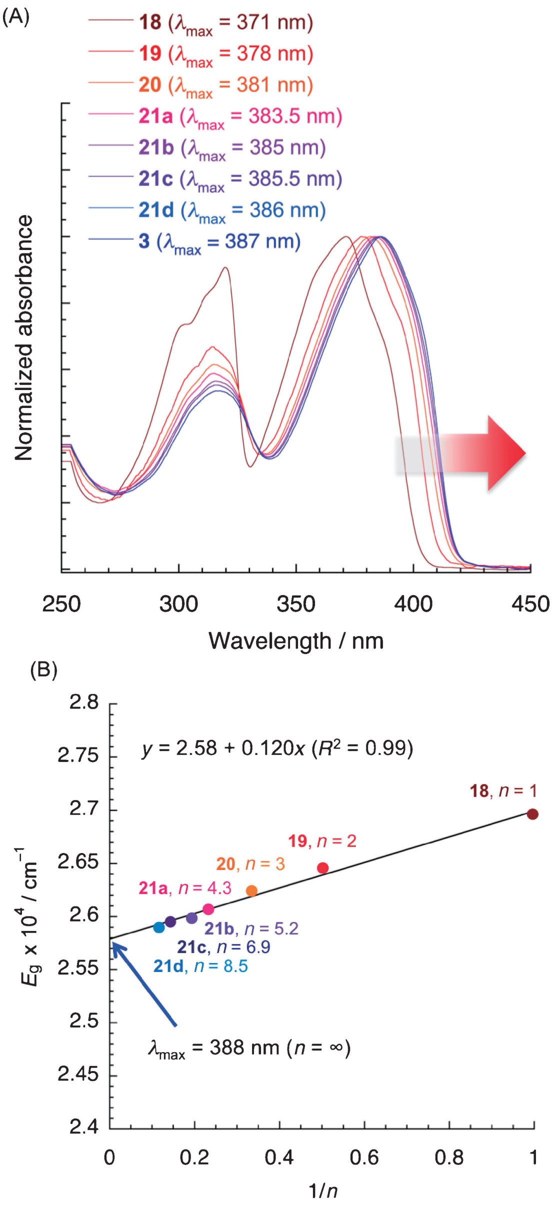


Figure 2. (A) UV–vis absorption spectra of compounds **18**–**20**, polymers **21a**–**21d** and **3** in $CHCl_3$ (1.0×10^{-5} M). (B) Correlation of the λ_{max} with $1/n$.

stacked fluorene units in the π-stacked poly(dibenzofulvene) extend to around five units.[23] In addition, the effective conjugation repeating unit of 7,7-diphenylnorbornane-based polymers was estimated to be four to five.[24] In both cases, π-stacked and flipped (unstacked) conformations are in equilibrium in a single polymer chain, and thus, four to five aromatic rings consist of the uniformly π-stacked sequence in solution. When [2.2]paracyclophane was incorporated into the conjugated polymer backbone, the π-electron systems were forced to stack on each other in proximity, thereby leading to a conformationally stable π-stacked structure. Therefore, in the [2.2]paracyclophane-containing conjugated polymer, electronic interactions extend through at least ten stacked AE moieties via the through-space conjugation in the ground state.

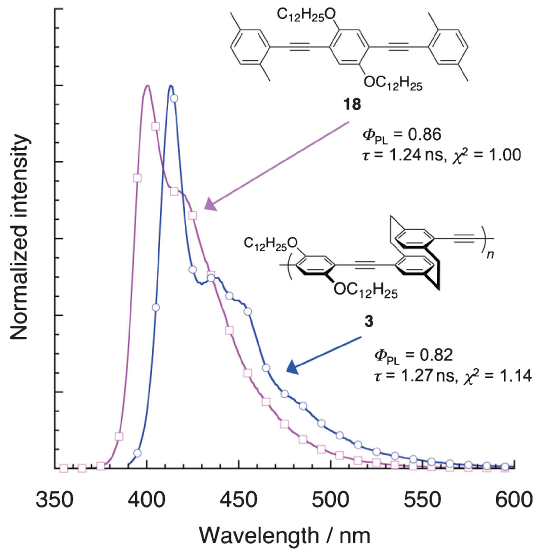


Figure 3. Photoluminescence spectra of polymer **3** and compound **18** in $CHCl_3$ (1.0×10^{-5} M) excited at each absorption maximum.

◆ *Emission Behaviors of π-Electron-system-layered Polymers*

Almost all the synthesized π-electron-system-layered polymers based on [2.2]paracyclophane exhibited photoluminescence (PL) in solution with high PL quantum efficiency (Φ_{PL}). For example, the Φ_{PL} values of PAE **3** and PAV **8** were calculated to be 0.82 and 0.70, respectively. Figure 3 shows the PL spectra of **3** and its stacked component **18** in $CHCl_3$ (1.0×10^{-5} M) upon excitation at the absorption maximum. Polymer **3** showed emission in the visible-blue region with a peak-top wavelength of 430 nm. Notably, the spectrum of **3** exhibited clear vibrational structures with a high Φ_{PL} of 0.82, which was similar to that of **18** ($\Phi_{PL} = 0.86$). Thus, the π-electron-system-layered polymers based on [2.2]paracyclophane did not exhibit broad spectra with a low Φ_{PL}, similar to excimer emission, although two dozen π-electron-systems are stacked in a single polymer main chain.

The emission behavior of [2.2]paracyclophane-based compounds was elucidated by Bazan, Mukamel, and co-workers.[14] Two types of emission mechanism—emission from "the monomer state" and emission from "the phane state (excimer-like emission)," which depend on the conjugation length of the stacked π-electron system and the extent of overlap between the stacked π-electron systems—were identified for [2.2]paracyclophane compounds. The PL spectra of **3** and **18** (Figure 3) and their high Φ_{PL} (0.82 for **3** and 0.86 for **18**) implied that emission of the polymer occurred from the monomer state and not from the phane state; this was further confirmed by fluorescence lifetime studies. Both fluorescence decay curves were found to be single exponential, and the fluorescence lifetime (τ) of the polymer was 1.27 ns ($\chi^2 = 1.14$), which was identical to the value of **18** ($\tau = 1.24$ ns, $\chi^2 = 1.00$).[20]

Recently, Jagtap and Collard reported the synthesis of π-electron-system-layered polymer **22** comprising pseudo-*geminal*-disubstituted [2.2]paracyclophane, in which the AE units are fully π-stacked in the polymer main chain (Figure 4).[23] The UV–vis absorption spectrum exhibited considerable tailing with the absorption edge at around 470 nm. The most remarkable difference between the optical properties of **3** and **22** was seen in the PL. The PL peak top in the case of **22** was observed at 530 nm, and the Stokes shift was approximately 170 nm; further the spectrum was broad and featureless, indicating emission of **22** arises from the phane state.

In order to verify the possibility of using π-electron-system-layered polymers as single molecular wires, in which energy and charge transfer can be effected via through-space interactions, we designed and prepared polymer **21e** ($M_n = 5400$, PDI = 3.0) end-capped with xylene rings and polymer **23** ($M_n = 6200$, PDI = 3.2) end-capped with anthracene rings (Scheme 6).[20] The M_n values indicated that **21e** comprised average seven AE layers and that **23** comprised average six AE units with two anthracene-containing AE units stacked at the polymer chain ends.

Before discussing the excited states of **21e** and **23**, it is necessary to investigate the UV–vis absorption spectra of these polymers as well as those of the π-stacked model compounds **18** and **24** in $CHCl_3$ (1.0×10^{-5} M). The spectrum of **18** exhibited π–π^* transition bands corresponding to the AE moiety at around 320 and 370 nm; the spectrum of **24**, however, exhibited an S_0–S_1 transition band corresponding to the anthracene ring over the range 390–470 nm, in addition to HOMO−1–LUMO and HOMO–LUMO+1 transition bands at 270 nm (Figure 5A). In the spectrum of **23**, absorption bands derived from both **18** and **24** were observed, as shown in Figure 5B.

In the PL spectra of **18** and **24** in $CHCl_3$ solutions (1.0×10^{-5} M; excited at each absorption maximum wave-

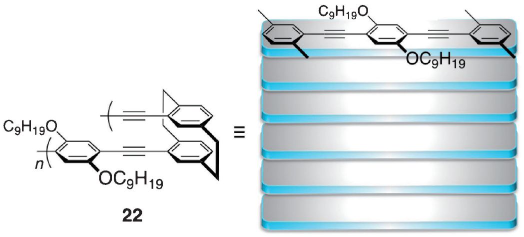


Figure 4. π-Electron-system-layered structure of polymer **22** comprising pseudo-*geminal*-disubstituted [2.2]paracyclophane.

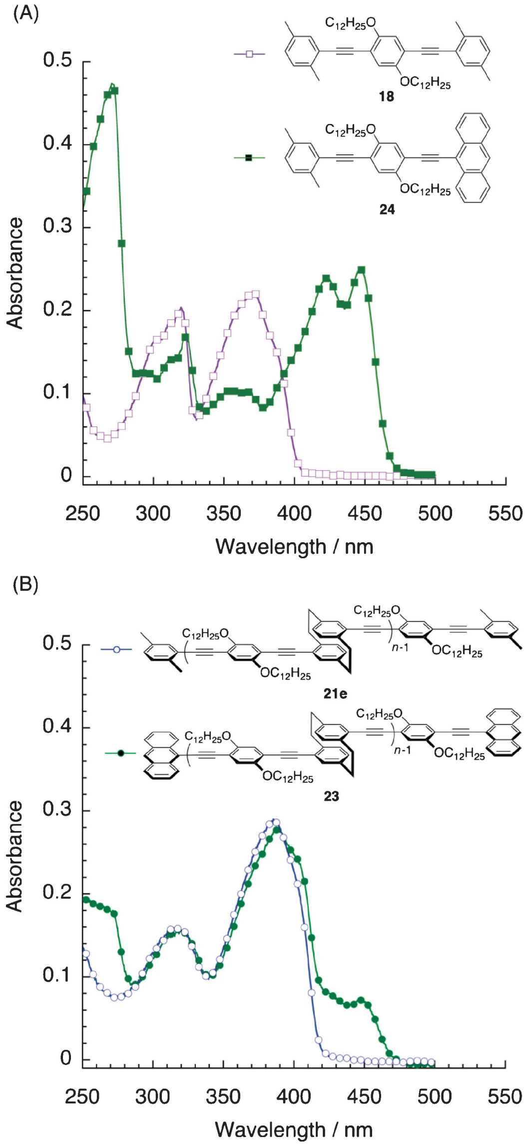
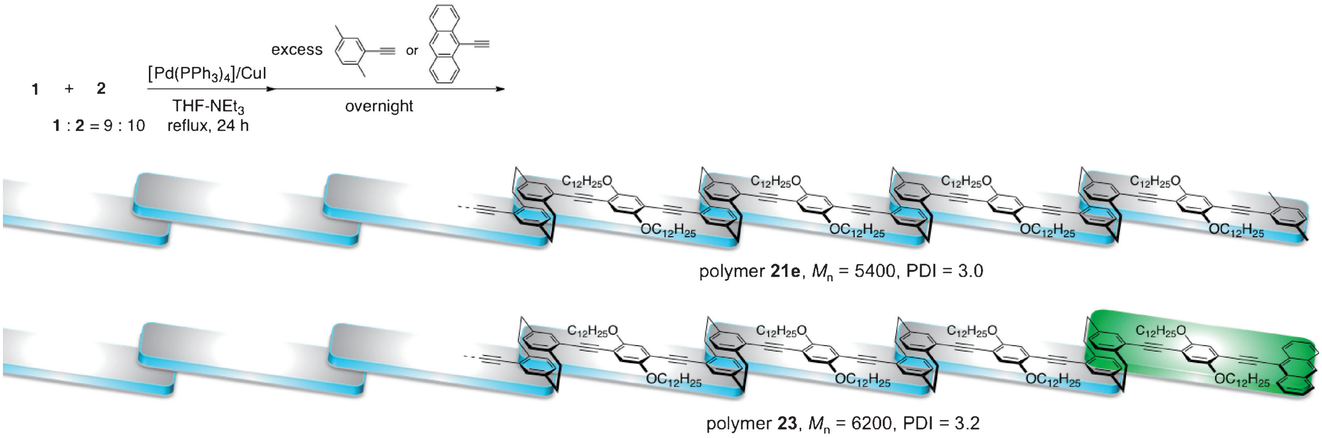


Figure 5. (A) UV–vis absorption spectra of compounds **18** and **24** in $CHCl_3$ (1.0×10^{-5} M). (B) UV–vis absorption spectra of polymers **21e** and **23** in $CHCl_3$ (1.0×10^{-5} M).



Scheme 6. Synthesis and illustration of π-electron-system-layered polymers **21e** and **23**.

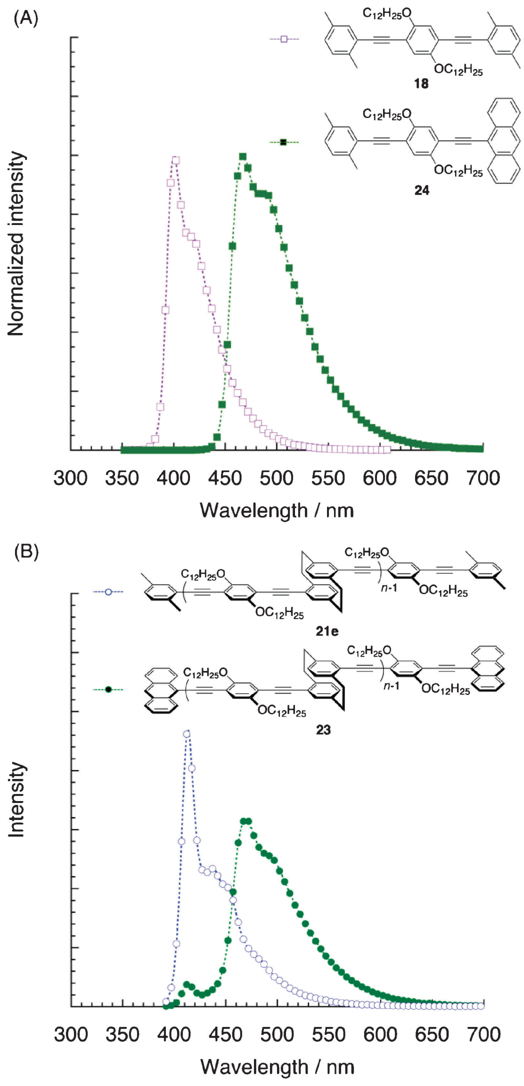


Figure 6. (A) Photoluminescence spectra of compound **18** in CHCl$_3$ (1.0×10^{-5} M) excited at 365 nm and compound **24** in CHCl$_3$ (1.0×10^{-5} M) excited at 468 nm. (B) Photoluminescence spectra of polymers **21e** and **23** in CHCl$_3$ (1.0×10^{-5} M) excited at 385 nm.

length, Figure 6A), peak maxima appeared at around 400 and 470 nm, respectively. PL emission occurred from the monomer state (vide supra) in the case of **21e**, as shown in Figure 6B, suggesting that the emission originated from the stacked AE units. In contrast, the spectrum of polymer **23** showed a small emission peak at around 410 nm and the main peak at around 470 nm (Figure 6B). Comparison of the spectra of **23** and **24** indicated that the peak at 470 nm was attributed to emission from the anthracene-containing π-electron systems at the termini. Figure 7 shows the time-resolved PL spectra of **23**; the intensity of the emission peak due to the stacked π-electron systems decreased, whereas that of the emission peak from the anthracene-containing π-electron systems increased. The strong overlap of the emission peak due to the stacked π-electron systems (at around 400 nm) with the absorption peak due to the anthracene-containing π-electron systems (390–470 nm) indicated fluorescence resonance energy transfer (FRET)[24] from the stacked π-electron systems to the terminal anthracene-containing π-electron systems.

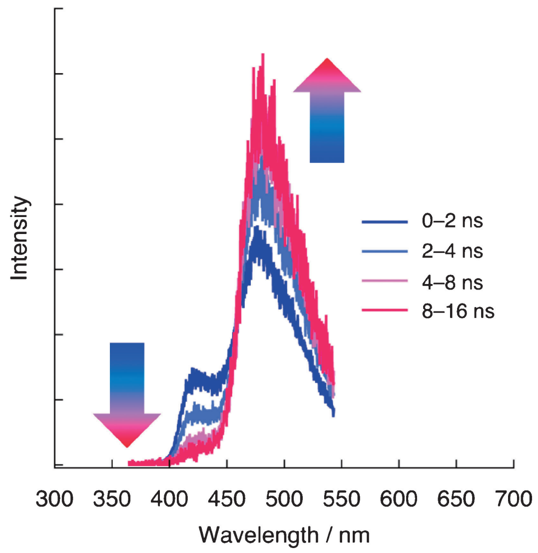
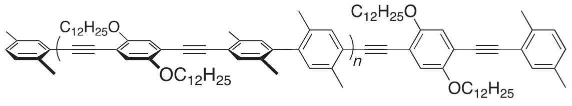


Figure 7. Time–resolved photoluminescence spectra of polymer **23** excited at 337 nm (N_2 laser) in CHCl$_3$ (1.0×10^{-6} M).



25 (M_n = 6800, PDI = 2.1)

Figure 8. Structure of polymer **25**.

The charge mobility in a single polymer chain of polymer **21e** was measured by the flash-photolysis time-resolved microwave conductivity (FP-TRMC) method and transient absorption spectroscopy (TAS) analysis of the photogenerated charged species.[25–27] Intramolecular charge mobility through the stacked π-electron systems in **21e** was superior to that through the twisted π-electron systems in **25** (Figure 8); this was because the conformational stability of the [2.2]paracyclophane-based stacked system caused a decrease in the reorganization energy.[20] These observations confirmed that π-electron-system-layered polymers based on [2.2]paracyclophane can function as single molecular wires that allow for unidirectional energy and charge transfer through the stacked π-electron systems.

♦ Conclusion and Outlook

In this article, we discussed the synthesis and optical properties of π-electron-system-layered polymers consisting of [2.2]paracyclophane in their main chain. Incorporation of the [2.2]paracyclophane skeleton into the conjugated polymer main chain afforded a new system in which individual π-electron systems were bridged by the paracyclophane units. Of note, the properties of the π-electron-system-layered polymers depended solely on the nature of the stacked π-electron system. We also demonstrated the through-space conjugation in the π-electron-system-layered polymers by adopting the oligomeric approach.

UV–vis absorption measurements showed a bathochromic shift of $\lambda_{\max}$ of the oligomers and polymers with an increase in the number of layered π-electron systems. [2.2]Paracyclophane forced the π-electron systems to stack partially on each other in proximity, which resulted in a conformationally stable π-stacked structure. Electronic interactions were effective through at least ten stacked π-electron systems in the ground state. PL studies revealed that emission occurs from the monomer state, and not from the phane state. The PL spectrum of the polymers showed a vibrational structure with high Φ_{PL}, and the fluorescence lifetime was short, although the polymer comprised two dozen stacked π-electron systems. Introduction of the designed π-electron systems to the polymer termini resulted in effective FRET from the stacked π-electron systems to the terminal π-electron systems.

As opposed to common π-conjugated polymers, which have a set of HOMO (valence band)–LUMO (conduction band) energy band gaps, the π-electron systems in the titled polymers had a single HOMO–LUMO energy band gap. Various aromatic groups can be incorporated into the [2.2]paracyclophane-containing polymers, and thus, energy and charge transfer along the polymer chain can be controlled by appropriate tuning of the band gap and energy level of the stacked π-electron system, respectively. The results of our study led us to conclude that π-electron-system-layered polymers based on [2.2]paracyclophane are the most promising candidates for single molecular wires, in which energy and/or charge transfer occurs via through-space interactions among the stacked π-electron systems.

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References

1 a) F. Vögtle, *Cyclophane Chemistry: Synthesis, Structures and Reactions*, John Wiley & Sons, Chichester, **1993**. b) *Modern Cyclophane Chemistry*, ed. by R. Gleiter, H. Hopf, Wiley-VCH, Weinheim, **2004**. doi:10.1002/3527603964. c) H. Hopf, *Angew. Chem., Int. Ed.* **2008**, *47*, 9808.

2 C. J. Brown, A. C. Farthing, *Nature* **1949**, *164*, 915.

3 D. J. Cram, H. Steinberg, *J. Am. Chem. Soc.* **1951**, *73*, 5691.

4 a) Y. Morisaki, Y. Chujo, *Angew. Chem., Int. Ed.* **2006**, *45*, 6430. b) Y. Morisaki, Y. Chujo, *Prog. Polym. Sci.* **2008**, *33*, 346.

5 Y. Morisaki, Y. Chujo, *Macromolecules* **2002**, *35*, 587.

6 S. Mizogami, S. Yoshimura, *J. Chem. Soc., Chem. Commun.* **1985**, 1736.

7 a) L. Guyard, P. Audebert, *Electrochem. Commun.* **2001**, *3*, 164. b) L. Guyard, P. Audebert, W. R. Dolbier, Jr., J.-X. Duan, *J. Electroanal. Chem.* **2002**, *537*, 189. c) F. Salhi, B. Lee, C. Metz, L. A. Bottomley, D. M. Collard, *Org. Lett.* **2002**, *4*, 3195. d) F. Salhi, D. M. Collard, *Adv. Mater.* **2003**, *15*, 81.

8 a) *Metal-Catalyzed Cross-Coupling Reactions*, ed. by F. Diederich, P. Stang, Wiely-VCH, Weinheim, **1998**. b) *Cross-Coupling Reactions: A Practical Guide* in *Topics in Current Chemistry*, ed. by N. Miyaura, Springer-Verlag, Berlin, **2002**, Vol. 219. doi:10.1007/3-540-45313-X. c) *Handbook of Organopalladium Chemistry for Organic Synthesis*, ed. by E.-i. Negishi, A. de Meijere, John Wiely & Sons, New York, **2002**. d) *Metal-Catalyzed Cross-Coupling Reactions*, ed. by A. de Meijere, F. Diedrich, Wiely-VCH, Weinheim, **2004**.

9 a) Y. Morisaki, Y. Chujo, *Chem. Lett.* **2002**, 194. b) Y. Morisaki, Y. Chujo, *Macromolecules* **2003**, *36*, 9319. c) Y. Morisaki, T. Ishida, H. Tanaka, Y. Chujo, *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 5891. d) Y. Morisaki, N. Wada, Y. Chujo, *Polymer* **2005**, *46*, 5884. e) Y. Morisaki, N. Wada, Y. Chujo, *Polym. Bull.* **2005**, *53*, 73. f) L. Lin, Y. Morisaki, Y. Chujo, *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 7003. g) Y. Morisaki, N. Wada, M. Arita, Y. Chujo, *Polym. Bull.* **2009**, *62*, 305.

10 a) Y. Tohda, K. Sonogashira, N. Hagihara, *Synthesis* **1977**, 777. b) K. Sonogashira, in *Handbook of Organopalladium Chemistry for Organic Synthesis*, ed. by E. Negishi, John Wiely & Sons, New York, **2002**, pp. 493–529.

11 L. Bondarenko, I. Dix, H. Hinrichs, H. Hopf, *Synthesis* **2004**, 2751.

12 a) Y. Morisaki, T. Ishida, Y. Chujo, *Macromolecules* **2002**, *35*, 7872. b) Y. Morisaki, Y. Chujo, *Macromolecules* **2004**, *37*, 4099.

13 a) T. Mizoroki, K. Mori, A. Ozaki, *Bull. Chem. Soc. Jpn.* **1971**, *44*, 581. b) R. F. Heck, J. P. Nolley, Jr., *J. Org. Chem.* **1972**, *37*, 2320.

14 a) W. J. Oldham, Jr., Y.-J. Miao, R. J. Lachicotte, G. C. Bazan, *J. Am. Chem. Soc.* **1998**, *120*, 419. b) G. C. Bazan, W. J. Oldham, Jr., R. J. Lachicotte, S. Tretiak, V. Chernyak, S. Mukamel, *J. Am. Chem. Soc.* **1998**, *120*, 9188. c) S. Wang, G. C. Bazan, S. Tretiak, S. Mukamel, *J. Am. Chem. Soc.* **2000**, *122*, 1289.

15 N. C. Greenham, S. C. Moratti, D. D. C. Bradley, R. H. Friend, A. B. Holmes, *Nature* **1993**, *365*, 628.

16 a) Y. Morisaki, L. Lin, Y. Chujo, *Chem. Lett.* **2009**, *38*, 734. b) Y. Morisaki, L. Lin, Y. Chujo, *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 5979.

17 a) Y. Morisaki, Y. Chujo, *Bull. Chem. Soc. Jpn.* **2005**, *78*, 288. b) L. Lin, Y. Morisaki, Y. Chujo, *Int. J. Polym. Sci.* **2010**, 908128.

18 a) N. Miyaura, K. Yamada, A. Suzuki, *Tetrahedron Lett.* **1979**, *20*, 3437. b) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457.

19 S. D. Walker, T. E. Barder, J. R. Martinelli, S. L. Buchwald, *Angew. Chem., Int. Ed.* **2004**, *43*, 1871.

20 Y. Morisaki, S. Ueno, A. Saeki, A. Asano, S. Seki, Y. Chujo, *Chem.—Eur. J.* **2012**, *18*, 4216.

21 a) T. Nakano, *Polym. J.* **2010**, *42*, 103. b) T. Nakano, K. Takewaki, T. Yade, Y. Okamoto, *J. Am. Chem. Soc.* **2001**, *123*, 9182. c) T. Nakano, T. Yade, *J. Am. Chem. Soc.* **2003**, *125*, 15474. d) T. Nakano, T. Yade, M. Yokoyama, N. Nagayama, *Chem. Lett.* **2004**, *33*, 296. e) T. Nakano, T. Yade, Y. Fukuda, T. Yamaguchi, S. Okumura, *Macromolecules* **2005**, *38*, 8140. f) T. Yade, T. Nakano, *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 561. g) T. Nakano, T. Yade, *Chem. Lett.* **2008**, *37*, 258. h) T. Nakano, M. Tanikawa, O. Nakagawa, T. Yade, T. Sakamoto, *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 239.

22 a) A. G. Martínez, J. O. Barcina, A. de Fresno Cerezo, A.-D. Schlüter, J. Frahn, *Adv. Mater.* **1999**, *11*, 27. b) J. O. Barcina, M. del Rosario Colorado Heras, M. Mba, R. G. Aspe, N. Herrero-García, *J. Org. Chem.* **2009**, *74*, 7148.

23 S. P. Jagtap, D. M. Collard, *J. Am. Chem. Soc.* **2010**, *132*, 12208.

24 Th. von Förster, *Naturwissenschaften* **1946**, *33*, 166.

25 a) G. P. van der Laan, M. P. de Haas, A. Hummel, H. Frey, S. Sheiko, M. Möller, *Macromolecules* **1994**, *27*, 1897. b) R. J. O. M. Hoofman, M. P. de Haas, L. D. A. Siebbeles, J. M. Warman, *Nature* **1998**, *392*, 54. c) J. M. Warman, G. H. Gelinck, M. P. de Haas, *J. Phys.: Condens. Matter* **2002**, *14*, 9935. d) F. C. Grozema, L. D. A. Siebbeles, J. M. Warman, S. Seki, S. Tagawa, U. Scherf, *Adv. Mater.* **2002**, *14*, 228. e) A. A. Kocherzhenko, S. Patwardhan, F. C. Grozema, H. L. Anderson, L. D. A. Siebbeles, *J. Am. Chem. Soc.* **2009**, *131*, 5522. f) P. Pingel, A. Zen, R. D. Abellón, F. C. Grozema, L. D. A. Siebbeles, D. Neher, *Adv. Funct. Mater.* **2010**, *20*, 2286.

26 a) A. Saeki, M. Tsuji, S. Seki, *Adv. Energy Mater.* **2011**, *1*, 661. b) A. Saeki, S. Seki, Y. Shimizu, T. Yamao, S. Hotta, *J. Chem. Phys.* **2010**, *132*, 134509. c) S. Prasanthkumar, A. Saeki, S. Seki, A. Ajayaghosh, *J. Am. Chem. Soc.* **2010**, *132*, 8866. d) Y. Yamamoto, G. Zhang, W. Jin, T. Fukushima, N. Ishii, A. Saeki, S. Seki, S. Tagawa, T. Minari, K. Tsukagoshi, T. Aida, *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 21051. e) A. Saeki, S. Seki, T. Takenobu, Y. Iwasa, S. Tagawa, *Adv. Mater.* **2008**, *20*, 920.

27 A. Saeki, T. Fukumatsu, S. Seki, *Macromolecules* **2011**, *44*, 3416.