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π-Electron-System-Layered Polymer: Through-Space Conjugation and Properties as a Single Molecular Wire

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Abstract: [2.2]Paracyclophane-based through-space conjugated oligomers and polymers were prepared, in which poly(*p*-arylene–ethynylene) (PAE) units were partially π-stacked and layered, and their properties in the ground state and excited state were investigated in detail. Electronic interactions among PAE units were effective through at least ten units in the ground state. Photoexcited energy transfer occurred from the stacked PAE units to the end-capping PAE moieties. The electrical conductivity of the polymers was estimated using the flash-photolysis time-resolved microwave conductivity (FP-TRMC) method and investigated together with time-dependent density functional theory (TD-DFT) calculations, showing that intramolecular charge carrier mobility through the stacked PAE units was a few tens of percentage larger than through the twisted PAE units.

Keywords: conjugation • molecular wires • paracyclophanes • polymers • time-resolved microwave conductivity

Introduction

Conjugated polymers are organic polymers that exhibit semiconducting behavior owing to the presence of π electrons, which are delocalized through the conjugated polymer backbone.[1] During the last two decades, these polymers have been widely regarded as highly promising candidates for next-generation optoelectronic materials. They combine the advantages of polymer technology, such as film-forming properties, processability, and light weight with light-emitting properties,[2] liquid crystallinity,[3] and electrical conductivity.[1,4] The properties of conjugated polymers significantly depend on the structures and properties of the aromatic moieties in the polymer main chain. The significant potential applications of these polymers, especially to optoelectronic materials, have motivated the development of next-generation conjugated polymer materials; as a result of the ever-increasing demands, it is important to explore the possibilities of developing novel conjugated polymers by incorporating various aromatic units into the conjugated polymer backbones.

In our studies, we have focused on cyclophane compounds as a new aromatic component of the conjugated polymers; in particular, a [2.2]paracyclophane skeleton has been introduced in their main chain by employing palladium-catalyzed coupling reactions. [2.2]Paracyclophane is attractive because it has a unique structure with two benzene rings stacked in proximity.[5] We have utilized [2.2]paracyclophane compounds as monomers for the conjugated polymers and have revealed the optical and electrochemical properties of the obtained polymers.[6] As shown in Figure 1, [2.2]paracyclophane enables the construction of π-electron systems that are constrained to stack on each other in the primary structure of the polymer chain. In general, almost all the conjugated polymers reported thus far are through-bond conjugated polymers comprising sp and/or sp^2 carbon frameworks, whereas through-space conjugated polymers comprising stacked π-electron systems have rarely been reported.[7–16] Therefore, it is important to obtain a better understanding of the characteristics of the through-space conjugated polymers. From this viewpoint, in this study, we have prepared [2.2]paracyclophane-containing through-space conjugated oligomers as well as polymers with end-capping units based on poly(*p*-arylene-ethynylene) (PAE).[17] In this paper, we report the through-space conjugation effect, energy transfer, and flash-photolysis time-resolved microwave conductivity (FR-TRMC) of the PAE-based through-space conjugated polymer. In this manner, the present work extends our previous studies and reveals new aspects of [2.2]paracyclophane-containing through-space conjugated polymers. Our investigations provide further insights into the potential applications of the through-space conjugated polymers to single molecular wires.

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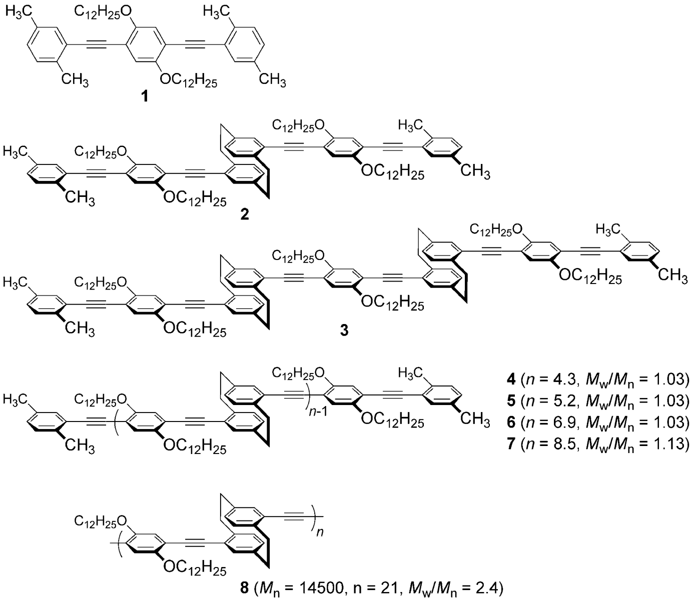


Figure 1. Structures of compounds **1**–**3**, oligomers **4**–**7**, and polymer **8**.

Results and Discussion

Through-space conjugated oligomers **1**–**3** and the polymer were synthesized by mainly Sonogashira–Hagihara coupling;[18] detailed synthetic procedures and the spectral data are given in Supporting Information. Furthermore, the obtained polymer was separated into four fractions by employing recyclable high-performance liquid chromatography (HPLC). The structures of oligomers **1**–**3**, separated polymers **4**–**7**,[19] and polymer **8** (the number-average molecular weight $M_n = 14\,500$ and weight-average molecular weight $M_w = 34\,500$) are shown in Figure 1. In oligomers **2**[20] and **3**, compound **1** is partially stacked in two and three layers, respectively; in addition, compound **1** is stacked in an average $n = 4.3$ layers in polymer **4**.

The normalized UV/Vis absorption spectra of **1**–**8** (1.0×10^{-5} M in $CHCl_3$) are shown in Figure 2 A. All the compounds exhibited typical absorption bands derived from the π–π* transition of the PAE moiety. The peak top wavelengths λ_{max} of **1**, **2**, and **3** were 371, 378, and 381 nm, respectively. Moreover, λ_{max} of the polymers gradually red-shifted as the number of layered PAE units (n) increased. The partially overlapped structure of the PAE units exhibited through-space interactions. In the present oligomers and polymers, the π stacking of the PAE units are perfectly ordered, which leads to ideal discussion about the conjugation length of this new class of through-space conjugated polymer.[21]

It is well established that λ_{max} of polymers with sufficiently high molecular weights (M_n) can be estimated from the relationship between the number of repeating π-conjugation units and λ_{max} for the π-conjugated oligomers.[22] This relationship was applied to the present through-space conjugation system. The peak top wavelengths (λ_{max} nm) of **1**–**7** were transformed into the energies (E_g in cm^{-1}), which were then plotted against the inverse of n (Figure 2 B). The linear correlation was reasonably good with the coefficient of determination (R^2) of 0.99. The spectrum of the through-space conjugated PAE should reach unity ($E_g = 25\,800$ cm^{-1}), when there are infinite layered units ($n = \infty$). This result is in good agreement with the experimental λ_{max} value of 387 nm for polymer **8** with $M_n = 14\,500$ and approximately 21 layered PAEs on an average. It is reported that the electronic interactions of the stacked aromatic units in the π-stacked polymer extend to around five fluorene units for poly(dibenzofulvene)[7c,23] and four to five benzene units for 7,7-diphenylnorbornane-based polymers[11,24] in the ground state. In both cases, π stacked and unstacked conformations are in equilibrium in a single polymer chain,[7,11] and the four to five aromatic units comprise the uniformly stacked sequence in solution. On the other hand, [2.2]paracyclophane forces the PAE units to stack on each other in proximity with *para*-substituted ethylene chains, which leads to a conforma-

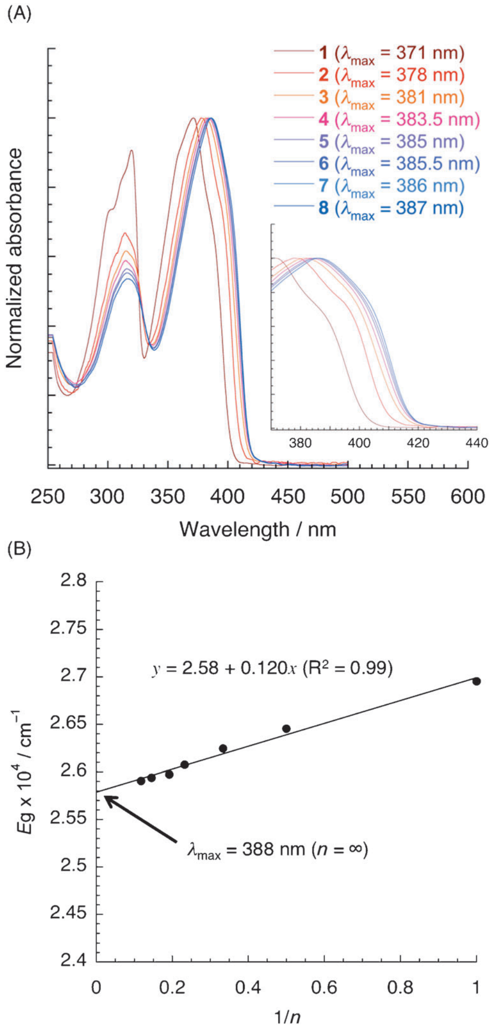
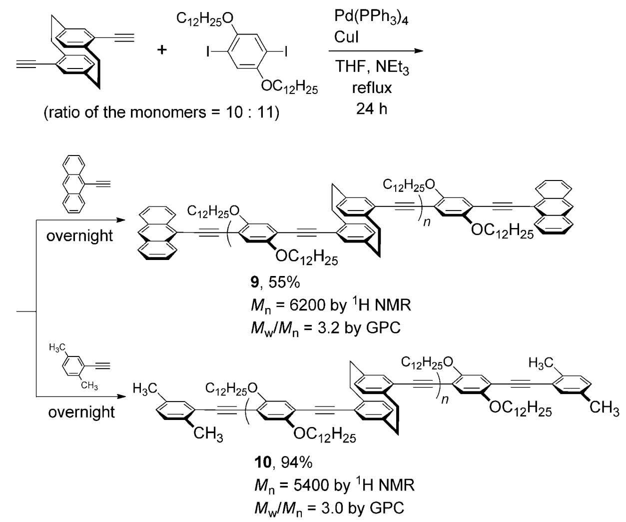


Figure 2. A) UV/Vis absorption spectra of **1**–**8** in $CHCl_3$ (1.0×10^{-5} M). B) Correlation of the λ_{max} of **1**–**7** with the invers number of the repeating units.

tionally stable π-stacked structure. Therefore, the [2.2]paracyclophane-containing through-space conjugated polymer exhibits improved through-space conjugation effects; UV/Vis absorption spectroscopy shows that the electronic interactions are effective through at least 10 stacked PAE moieties in the ground state.[25]

We also synthesized through-space conjugated polymer **9** with anthracenes as end-capping groups by Sonogashira–Hagihara coupling, as shown in Scheme 1. In addition, polymer **10** end-capped with xylene was synthesized again using the same procedure (Scheme 1). The ratio of the monomers pseudo-*para*-diethynyl [2.2]paracyclophane and 2,5-didodecyloxy-1,4-diiodobenzene was 10:11. The polymerization was monitored by gel permeation chromatography (GPC) (Figure S14 in Supporting Information), and after 24 h, 9-ethynylanthracene and ethynylxylene were added to the reaction mixture to obtain polymers **9** and **10**, respectively.



Scheme 1. Synthesis of polymers **9** and **10**.

The structures of polymers **9** and **10** were confirmed by ^{1}H and ^{13}C NMR spectra; Figure 3 shows the ^{1}H NMR spectrum of **9** as a representative example. In Figure 3, the signals attributable to dodecyl protons can be observed at 0.9–2.0 ppm, and the signals of the methylene unit -OCH_2- in the dodecyloxy group were downfield shifted to 4.2 ppm. The signals for inequivalent cyclophane bridge methylene protons were observed from 2.9 to 3.8 ppm, and those corresponding to the cyclophane and phenylene protons were observed at 6.5–7.2 ppm. Finally, the peaks attributable to anthracene protons appeared at 7.5–8.8 ppm. The M_n of **9** was estimated from the ^{1}H NMR integral ratio between anthracene and cyclophane bridge methylene protons to be 6200, indicating that an average of eight PAE units were stacked in the polymer primary chain; in other words, six PAE units were layered, and two anthracene-containing PAE units were stacked at the polymer termini. In addition, M_n of **10** was estimated to be 5400 with an average stacking of 7 PAE units.

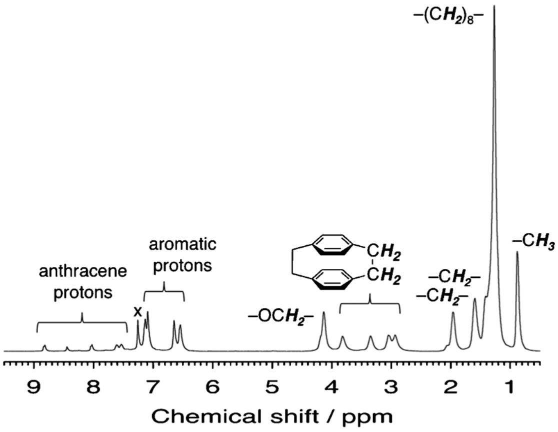


Figure 3. ^{1}H NMR spectra of polymer **9**, 400 MHz, $CDCl_3$.

Figure 4 A shows the UV/Vis absorption spectra of **9** and **10** in $CHCl_3$ (1.0×10^{-5} M). Both this Figure and Figure 2 A indicate that polymer **10** exhibited absorption bands at around 380 and 320 nm; this was a result of the π–π* transition of PAE moiety. On the other hand, polymer **9** exhibited two additional absorption bands at around 450 and 250 nm (Figure 4 A). These two bands can be assigned to the absorption of the end-capping anthracene moiety by analyzing the UV/Vis absorption spectra of model compounds **1** and **11** that represent the end-capping π-electron system of polymer **9** (Figure 4 B); in other words, the absorption spectrum of **9** consists of the absorption spectra of **1** and **11**.

The fluorescence emission spectra of **9** and **10** in $CHCl_3$ (1.0×10^{-5} M; excited at 385 nm) are shown in Figure 5 A. We confirmed that this concentration (1.0×10^{-5} M) was sufficiently diluted to avoid intermolecular interactions among the polymers as a result of the concentration effect (Figures S31 and S32 in the Supporting Information). In the case of **10**, an emission peak with a vibrational structure was observed at around 410 nm, and the fluorescence quantum efficiency (Φ_{FL}) was 0.82; this is similar to the spectrum of **1** with an emission peak at around 400 nm and Φ_{FL} value of 0.86 (Figure 5 B). The through-space conjugated polymers emit from the chromophore state rather than the phane (excimer-like) state (vide infra),[20,26] and the emission of **10** occurs from each stacked π-electron system of **1**.

On the other hand, the spectrum of **9**, with anthracene-containing π-electron systems at the polymer termini, was very different from that of **10**. The emission from the stacked π-electron systems in **9** clearly decreased even though they were efficiently excited at 385 nm, while there was an emission peak at around 470 nm with Φ_{FL} value of 0.70. This new emission peak for **9** was a result of the photoluminescence from the end-capping π-electron systems in contrast to the case of the emission spectrum of model compound **11** (Figure 5 B). The time-resolved fluorescence spectra of **9** show that the emission from stacked π-electron systems decreased, whereas that from the end-capping π-elec-

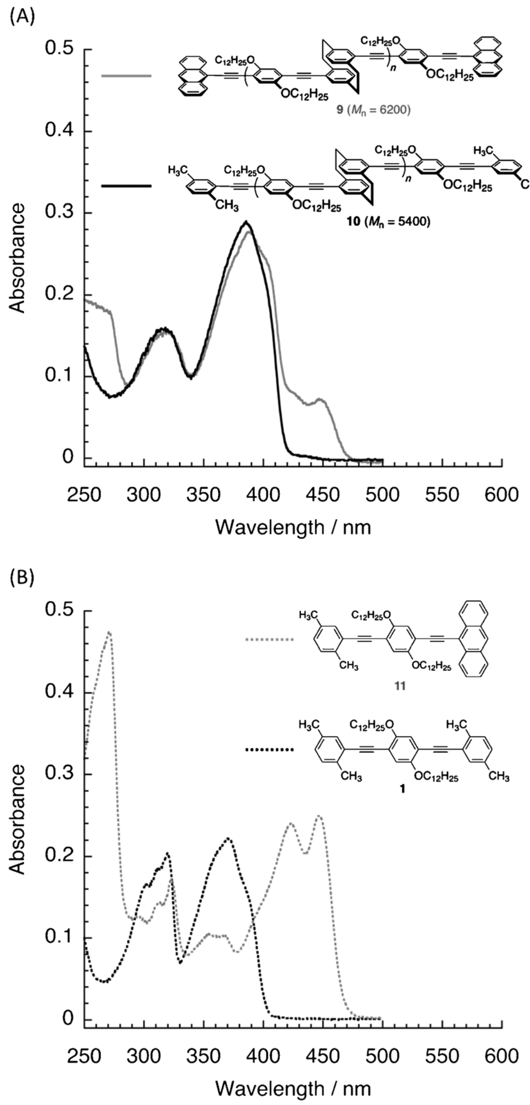


Figure 4. A) UV/Vis absorption spectra of polymers **9** and **10** in $CHCl_3$ (1.0×10^{-5} M). B) UV/Vis absorption spectra of compounds **1** and **11** in $CHCl_3$ (1.0×10^{-5} M).

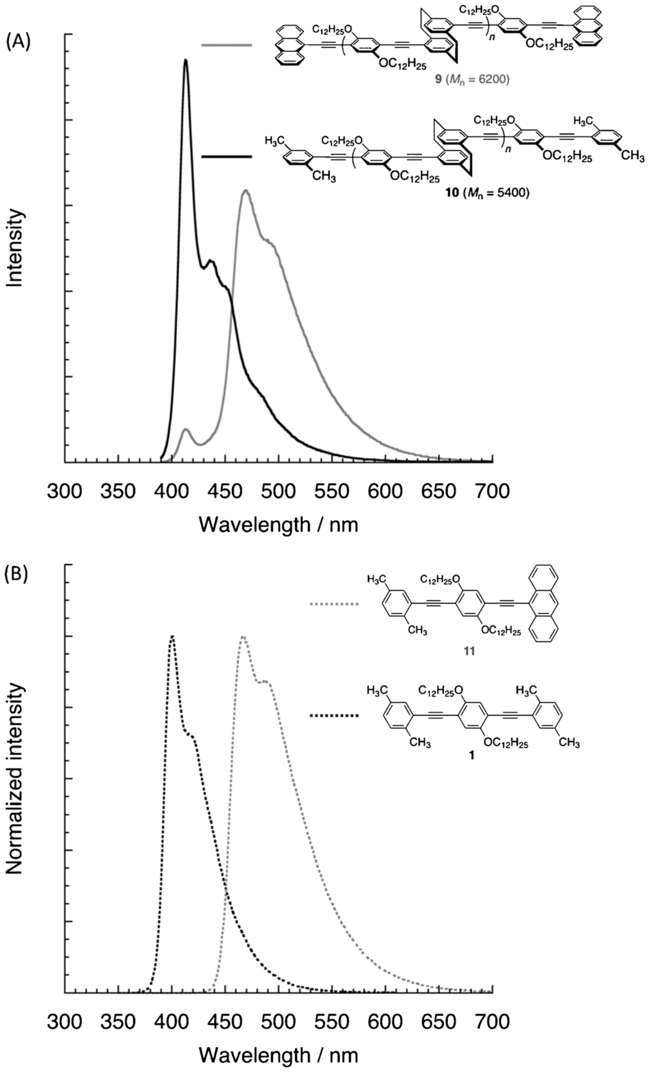


Figure 5. A) Fluorescence emission spectra of polymers **9** and **10** in $CHCl_3$ (1.0×10^{-5} M) excited at 385 nm. B) Fluorescence emission spectra of compound **1** in $CHCl_3$ (1.0×10^{-5} M) excited at 365 nm and compound **11** in $CHCl_3$ (1.0×10^{-5} M) excited at 468 nm.

tron systems increased simultaneously, as shown in Figure 6. Since the emission peak of the stacked π-electron systems overlapped well with the absorption peak of the anthracene-containing π-electron systems, fluorescence resonance energy transfer (FRET)[27] occurred from the stacked π-electron systems to the end-capping π-electron systems.

Fluorescence lifetime measurements were conducted for compounds **1** and **11** as well as polymers **9** and **10**; their decay curves are shown in Figure 7. Compounds **1** and **11** in $CHCl_3$ (1.0×10^{-6} M) exhibited single-exponential fluorescence decay, and the calculated lifetimes (τ) were 1.24 ns and 2.71 ns, respectively. The decay curve of **10** in $CHCl_3$ (1.0×10^{-6} M) could be fitted to a single-exponential equation; the calculated τ was 1.27 ns, which was almost identical to $\tau=1.24$ ns for **1**. This result clearly supports our observations that the through-space conjugated polymer emits from the chromophore state rather than the phane state (vide supra). In addition, the emission behaviors of [2.2]paracyclophane-based stilbenoid dimers have been well established by Bazan and co-workers;[20,26] the behavior of our polymer is consistent with that of the stilbenoid dimer.[26b] On the other hand, the fluorescence curve of **9** in $CHCl_3$ (1.0×10^{-6} M) was found to be a double exponential, and the decay was dominated by a component of $\tau=2.31$ ns. This value and decay curve were similar to those of **11**, and this suggests that the main emission from **9** can be attributed to the emission of the anthracene-containing π-electron systems at the polymer termini.

The electrical conductivity of the through-space conjugated polymer was investigated by the non-contact measurement technique using the flash-photolysis time-resolved microwave conductivity (FP-TRMC) method.[28–30] To obtain the charge mobility through a single polymer chain, polymer **10** ($M_n=5400$, 1 mg) was dispersed in a polystyrene ($M_w=$

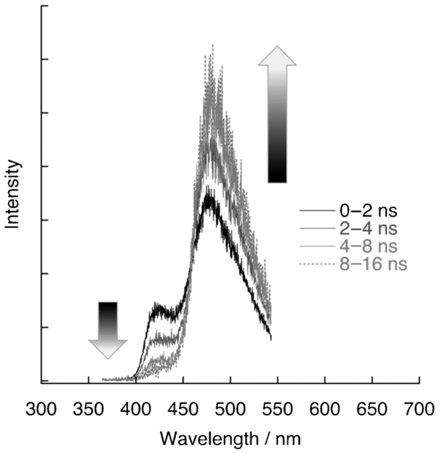


Figure 6. Time-resolved fluorescence emission spectra of polymer **9** excited at 337 nm (N_2 laser) in $CHCl_3$ (1.0×10^{-6} M).

10×10^6; 100 mg) film without any dopants.[31] The cast film on quartz was excited by a laser pulse at 355 nm, and kinetic traces of microwave conductivity transients were obtained as shown in Figure 8 A. The product of the photo carrier generation yield (ϕ) and the sum of charge mobilities ($\Sigma\mu$) was estimated to be 1.9×10^{-5} cm^{2}V^{-1}s^{-1} at the peak. In some cases, a ϕ value can be determined by transient absorption spectroscopy (TAS) of photo-generated charged species. We therefore conducted TAS of polystyrene-bound **10** film and found the transient absorption spectrum with a peak at around 570 nm (Figure 8 B). This absorption is, however, attributed to a triplet excited state of **10** (vide infra).

The similar measurement was carried out for polymer **12** ($M_n=6800$) in which compound **1** was linearly connected and twisted (Figure 10). The photoconductivity kinetics and the $\phi\Sigma\mu$ maximum value (1.9×10^{-5} cm^{2}V^{-1}s^{-1}) of **12** were the same as those of **10** (Figure 9), suggesting that the stacked and linear polymers have comparable charge carrier transport property. The TAS intensity of **12** was about three times higher than **10**, while the peak and the shape were almost identical (centered at 560 nm).

In order to assign the transient absorption observed for **10** and **12** diluted in a polystyrene matrix, we performed TAS on solutions of **10** and **12** in Ar- or air-bubbled toluene . The almost identical absorption spectra with those in polystyrene matrices were obtained in the Ar-bubbled solutions, for which the absorption peaks were located at 580 and 550 nm for **10** and **12**, respectively.[32] These absorptions were significantly suppressed by air bubbling, due to the quenching by O_2. Time-dependent density functional theory (TD-DFT) calculation of the dimers showed that the photoabsorptions of triplet excited states and their oscillator strengths (f) of **10** and **12** were 622 ($f=1.56$) and 550 nm ($f=2.38$), respectively,[33] which are in good coincidence with the experiments. Considering the observed lifetime (ca. 10–20 μs), quenching by O_2, and TD-DFT results, we concluded that the transient absorptions in both toluene solutions and polystyrene matrices are attributed mainly to the triplet excited state.

On the basis of extinction coefficient calculated from the spectrum fitting and calculated oscillator strength,[33,34] the triplet yields of **10** and **12** in polystyrene matrices generated upon exposure to a 355 nm nanosecond laser were estimated to be 6.1×10^{-3} and 8.7×10^{-3}, respectively.[33] This suggests that the photo charge carrier generation yields (ϕ) of **10** and **12** are on the same order and much smaller than triplet yield. This presumption is corroborated by the direct-photocurrent measurements of pristine **10** and **12** polymers using a comb-type electrode,[30] where the integrated photocurrents at fixed applied voltage (e.g., 2×10^4 V cm^{-1}) also indicated the values on the same order (3.6 pC for **10** and 4.8 pC for **12**).[35] From the FP-TRMC, TAS, and photocurrent measurements, it is of interest to note again that **10** (through-space conjugated PAE) and **12** (twisted PAE) possesses comparable charge carrier transport property. On a closer look at the triplet yields and direct-photocurrent measurements, these values of **10** tend to be smaller than **12**, suggesting that intramolecular charge carrier mobility of **10** is a few tens of percentage larger than **12**.

Figure 11 presents the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of neutral state of **10** and **12** dimers obtained by the DFT calculations. Both of the molecules show the delocalized HOMO and LUMO over the two repeating units. The singly-occupied molecular orbital (SOMO) of radical cations are also delocalized in the similar manner; however, the dihedral angle of **12** at the twisted point (indicated by an arrow in the figure) was reduced from 88.9° for the neutral state to 56.9° for radical cation. Such a planarization of polymer backbone has been reported as well for the neutral and radical cationic states of polyfluorene,[30,36] facilitating the delocalization of the charges. In contrast, the structure of **10** did not change significantly between neutral and cationic states, while its SOMO is evidently delocalized through the space at not only the center cyclophane unit but also the end cyclophane units. The rigidity of the main chain of **10** can decrease the reorganization energy for the charge transport,[37] which contributes to the increase of intramolecular charge carrier mobility. We are currently investigating the dependence of the conductivity in a single polymer chain of the through-space conjugated polymer on the chain length by employing a well-defined oligomer with electron-acceptor units such as fullerene[38] and/or perylene[39] derivatives at the polymer chain ends. Considering the recent report on the molecular junction behavior of [2.2]paracyclophane-based oligophenylenevinylens,[40] [2.2]paracyclophane-based through-space conjugated oligomers and polymers can be potentially applied in the molecular wire transporting charges and energy in one direction.

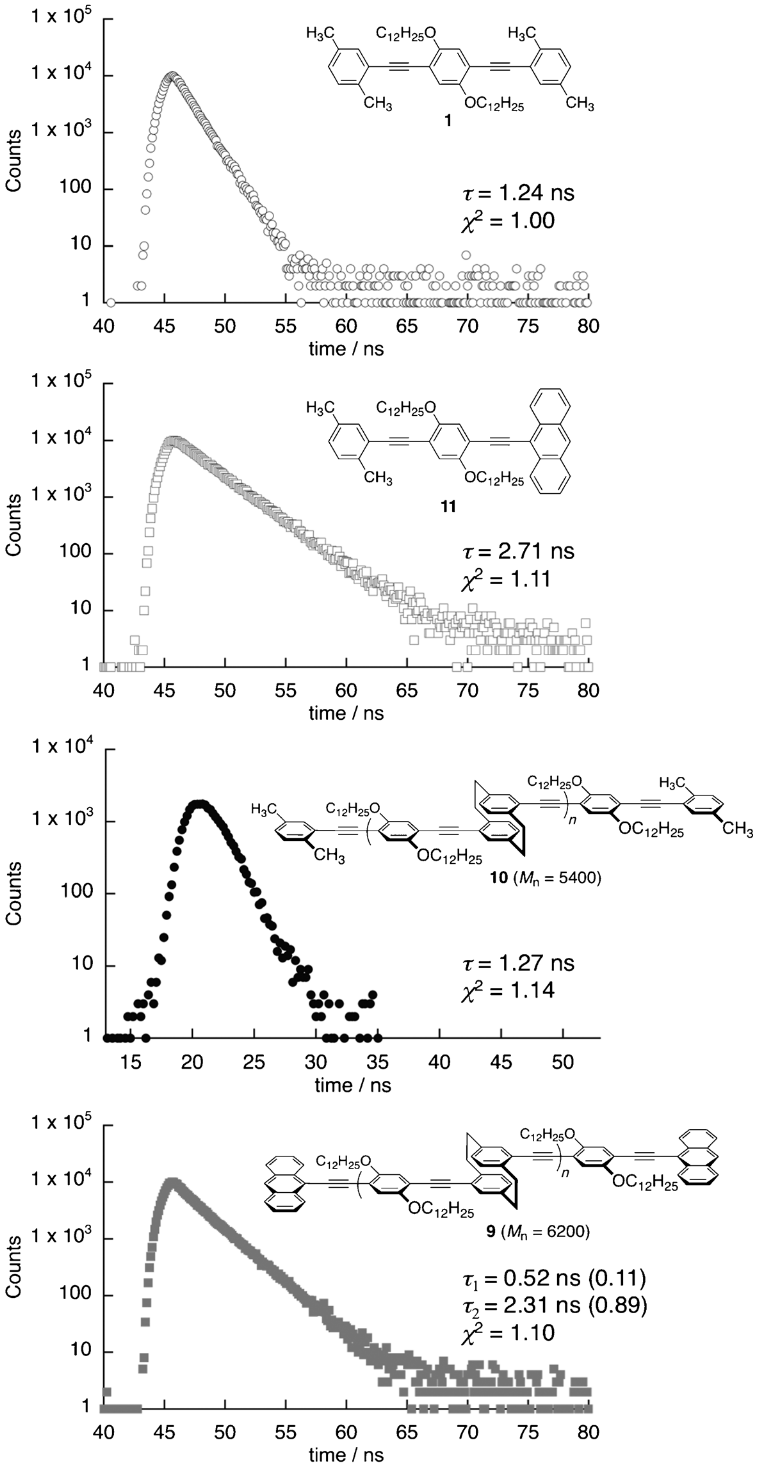


Figure 7. Fluorescence decay curves and data of compound **1** in $CHCl_3$ (1.0×10^{-6} M) excited at 373 nm with LED laser, compound **11** in $CHCl_3$ (1.0×10^{-6} M) excited at 373 nm with LED laser, polymer **10** in $CHCl_3$ (1.0×10^{-6} M) excited at 337 nm with N_2 laser, and polymer **9** in $CHCl_3$ (1.0×10^{-6} M) excited at 373 nm with LED laser.

Conclusion

We synthesized PAE-based [2.2]paracyclophane-containing through-space conjugated oligomers in which two and three PAE units were stacked in proximity. The incorporation of the [2.2]paracyclophane unit into the main chain of the conjugated polymer constructed the PAE unit and formed its partially overlapped structure. We also synthesized [2.2]paracyclophane-containing through-space conjugated polymers with xylene groups as the end-capping units. In the UV/Vis absorption spectra, λ_{max} of the oligomers and polymers were gradually red-shifted as the number of layered PAE units increased. [2.2]Paracyclophane forces the PAE units to stack on each other in proximity, leading to a stable π-stacked structure. Therefore, in the polymer, electronic interactions were effective through at least ten stacked PAE units in the ground state.

A through-space conjugated polymer with anthracene groups as the end-capping groups was also synthesized. Since the emission peak of the stacked PAEs and the absorption band of the anthracene-containing PAE end-capping units overlapped well, FRET occurred from the stacked π-electron systems to the end-capping PAEs. The electric conductivity of the through-space conjugated polymer was measured by the TRMC-TAS method and investigated together with the TD-DFT calculation. The intramolecular charge mobility through the stacked π-electron systems was a few tens of percent larger than that through the twisted π-electron systems, owing to the decrease of the reorganization energy by the rigidity of the through-space conjugated polymer main chain composed of [2.2]paracyclophane.

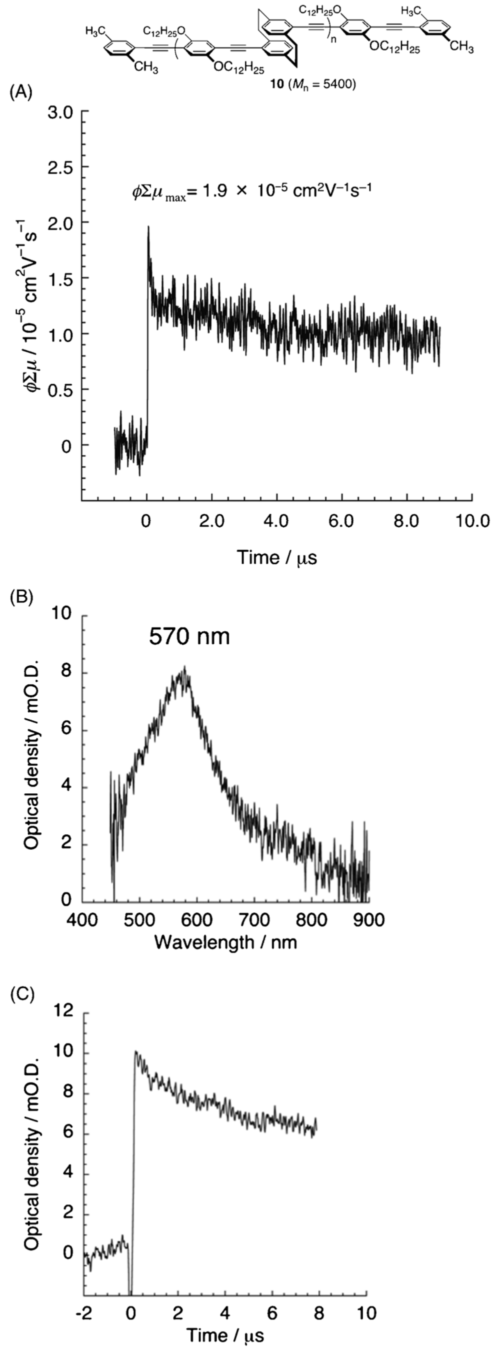


Figure 8. A) TRMC conductivity transient of polymer **10** in the polystyrene film on a quartz under the excitation at 355 nm (1.8×10^{16} photons cm^{-2}). B) Transient absorption spectrum of polymer **10** in the polystyrene film on a quartz. C) Kinetic profile at 570 nm.

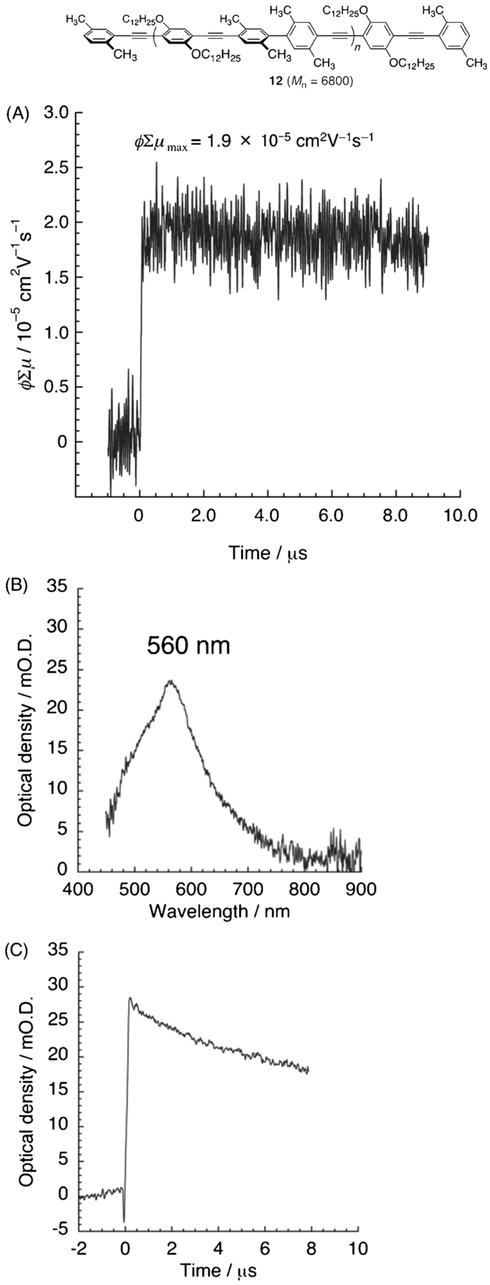


Figure 9. A) TRMC conductivity transient of polymer **12** in the polystyrene film on a quartz under the excitation at 355 nm (1.8×10^{16} photons cm^{-2}). B) Transient absorption spectrum of polymer **12** in the polystyrene film on a quartz. C) Kinetic profile at 560 nm.

In [2.2]paracyclophane-containing through-space conjugated oligomers and polymers, each layered π-electron system possesses a frontier orbital; therefore, each bandgap energy and energy level can be controlled by making appropriate choices of the co-monomer of the [2.2]paracyclophane monomer. The band-gap energy gradient leads to unidirectional energy flow, and HOMO or LUMO energy level gradients make it possible to transfer electrons or holes unidirectionally. The design and synthesis of such [2.2]paracyclophane-containing single molecular wires are currently in progress.

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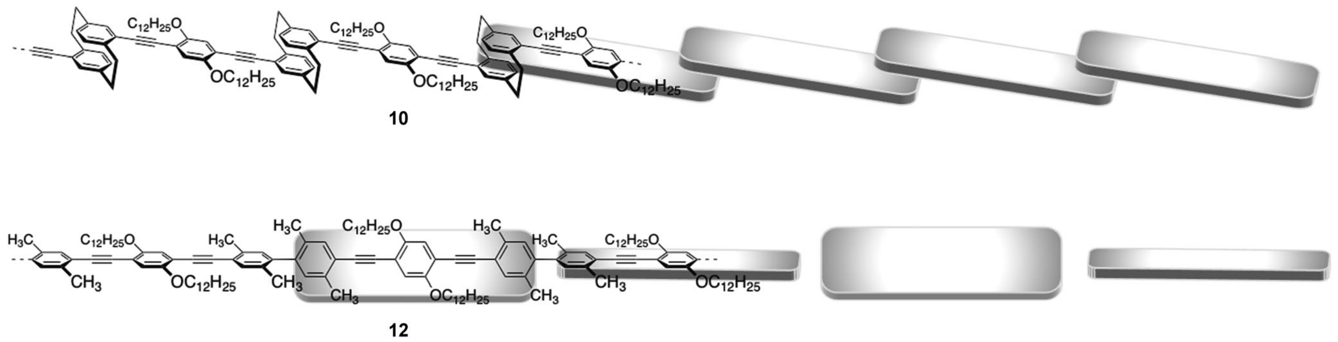

Figure 10. π-Stacked structure of polymer **10** and twisted structure of polymer **12**.

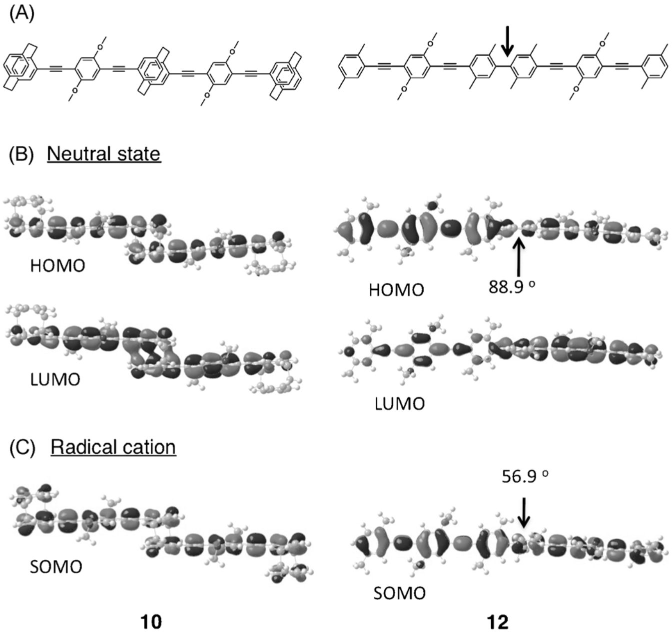

Figure 11. A) Dimer model structures of **10** and **12** for DFT calculation using B3LYP/6-31G(d,p). B) HOMO and LUMO of neutral states. C) SOMO of radical cations.

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