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Award Accounts

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Synthesis of π-Stacked Polymers on the Basis of [2.2]Paracyclophane

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We synthesized π-stacked polymers by incorporating [2.2]paracyclophane units into conjugated polymer backbones and developed corresponding through-space-conjugated polymers and aromatic-ring-layered polymers. We also synthesized [2.2]paracyclophane-containing polyamidoamine (PAMAM) dendrimers and optically active polymethylenes. These polymers and dendrimers are the first well-defined and well-characterized conjugated polymers with cyclophane units in their main chain. We studied the properties of the [2.2]paracyclophane-containing through-space-conjugated polymers. We demonstrated the use of these through-space-conjugated polymers in optoelectronic applications such as an EL device. Further, we developed a synthetic strategy for new π-stacked polymers comprising layered aromatic rings on a xanthene skeleton as the scaffold. The occurrence of fluorescence resonance energy transfer from the layered cyclophanes to the end-capping aromatic moieties was verified.

1. Introduction

Over the last three decades, conjugated polymers, such as poly(arylene)s, poly(arylenevinylene)s, and poly(aryleneethynylene)s, have been at the forefront of polymer research.[1] The growing interest in these polymers is attributed to their unique optical and electronic properties in addition to other advantageous features such as low weight, softness, processability, and film-forming ability. These properties strongly depend on the nature of the repeating aromatic unit in the conjugated polymers. Therefore, the design and synthesis of novel conjugated polymers having unique aromatic systems are of importance in developing next-generation organic polymer materials.

In general, conjugated polymers consist of aromatic rings connected to each other via carbon–carbon single, double, and triple bonds. Needless to mention, polymers such as polyacetylenes[2] and carbines,[3] which consist of only carbon–carbon double bonds and triple bonds, respectively, are also conjugated polymers. Almost all the conjugated polymers reported thus far are through-bond-conjugated polymers comprising sp or sp^2 carbons; only a few studies have been conducted on through-space-conjugated polymers comprising π-stacked aromatic systems.[4]

In organic polymer materials, charge (hole and electron) and energy transfers occur via through-space interactions among π-conjugated systems, such as the aromatic rings in conjugated polymers. For example, in an organic electroluminescence (EL) device, holes and electrons travel a distance of approximately one hundred nanometers by a hopping mechanism. The presence of a π-stacked structure and the orientation of the aromatic rings play an important role in the occurrence of effective charge or energy transfers in a polymeric system. It has been recognized that the construction of suitable higher ordered structures of conjugated polymers used in optoelectronic devices is important for enhancing the device performance. However, the construction and incorporation of π-stacked structures such as layered aromatic rings into a single polymer chain have not been extensively studied in polymer chemistry.[4] The resultant aromatic-ring-layered polymers synthesized by the above-mentioned approach are expected to have superior conductivity and/or charge mobility than the existing polymer materials. In addition, conjugated polymers consisting of one-dimensionally layered aromatic rings can be used as single molecular wires, where the effective charge and/or energy transfers occur via through-space interaction.

During the course of our studies on conjugated polymers, we focused our attention on cyclophane compounds with π-stacked benzene rings and synthesized a novel through-space-conjugated polymer containing cyclophane units in its main chain.[5] In this paper, we mainly discuss the synthesis of [2.2]paracyclophane-based polymers with π-stacked structures. First, we discuss the through-space-conjugated polymers containing [2.2]paracyclophane in the main chain, and then, discuss the dendrimers and polymers containing [2.2]paracyclophane. We have also synthesized dithia[3.3]metaphane-containing polymers;[6] however, the discussion of these polymers has not been included in this paper, because the characteristics of the dithia[3.3]metaphane-containing polymers are determined by the conformational flexibility of the

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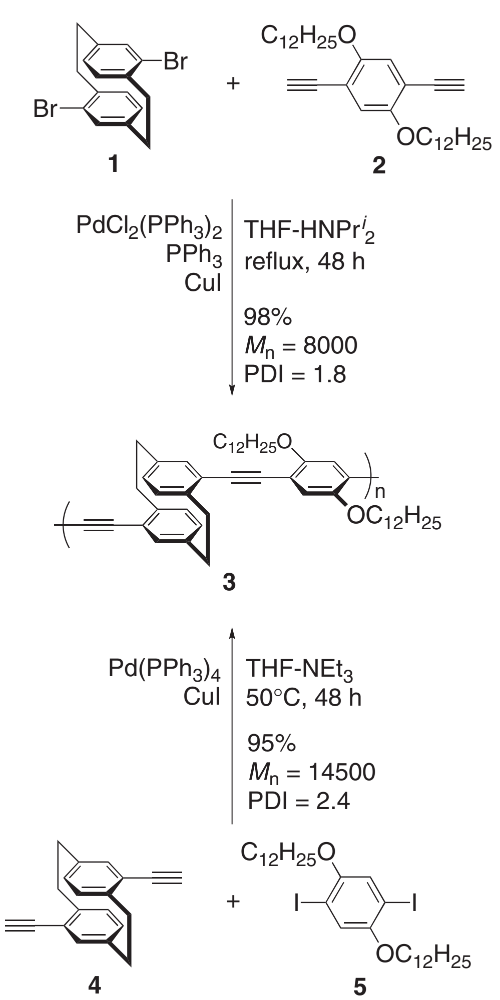
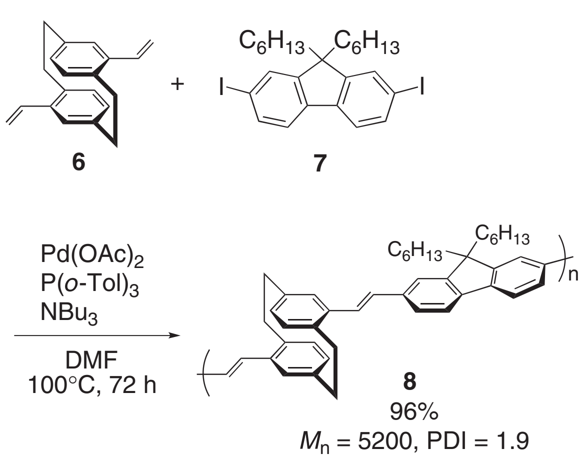
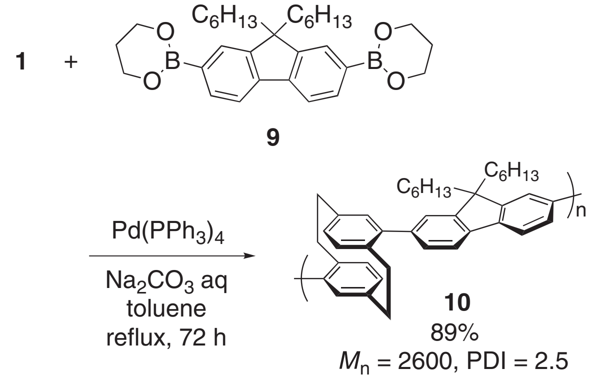


Scheme 1.



Scheme 2.



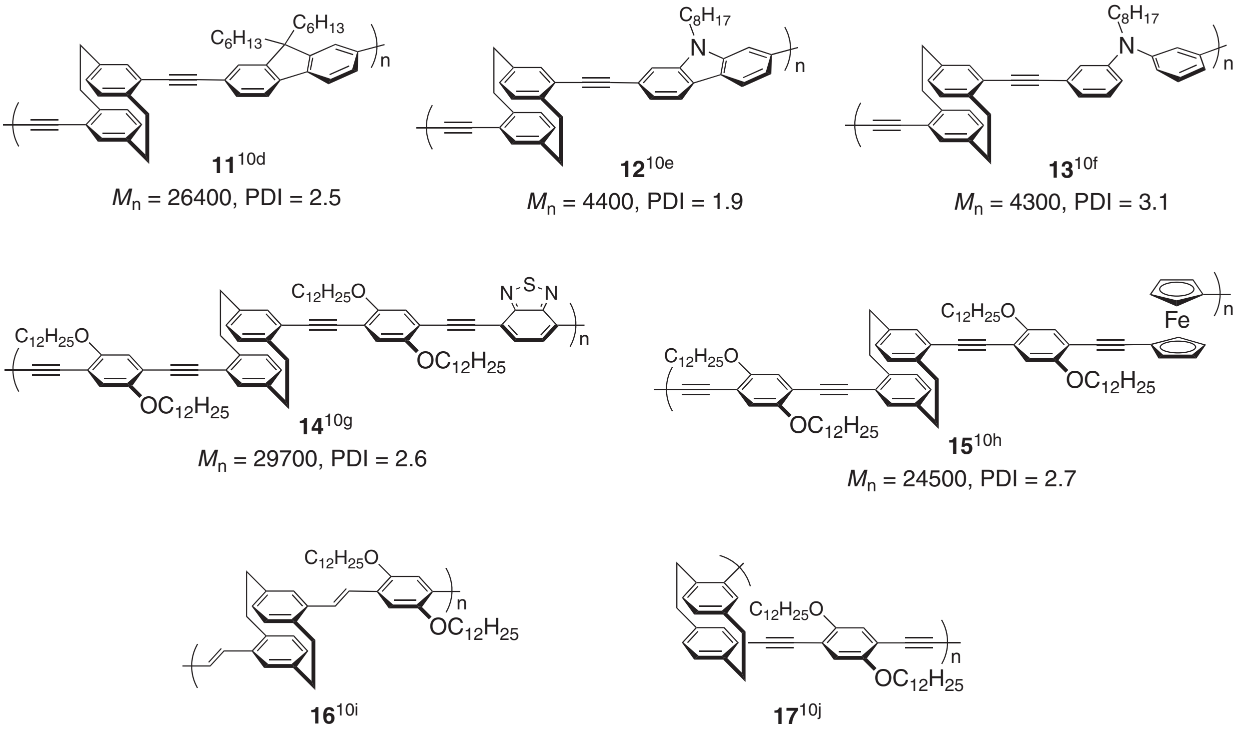
Scheme 3.

dithia[3.3]metaphane unit. In the final section of this paper, we discuss the characteristics of aromatic-ring-layered polymers comprising [2.2]paracyclophane units on a xanthene skeleton.

2. Synthesis of [2.2]Paracyclophane-Based Through-Space-Conjugated Polymers

It is important to note that most of the characteristic features of [2.2]paracyclophane compounds are attributed to the π-stacked structure, which comprises two parallel benzene rings on top of each other. Since the synthesis of the first [2.2]paracyclophane compound in 1949,[7] the functionalization and physical properties of [2.2]paracyclophane have attracted considerable attention in the field of organic chemistry.[8] However, the use of [2.2]paracyclophane compounds as a main-chain constituent of polymers remains fairly unexplored.[5b] In fact, at the onset of our study of through-space-conjugated systems, only one conjugated polymer containing [2.2]paracyclophane as a repeating unit in the main chain was known.[9a] This [2.2]paracyclophane polymer was obtained by the electrochemical polymerization of thiophene-substituted [2.2]paracyclophane in a cyclic voltammetry (CV) cell. The polymer was insoluble in almost all organic solvents and its characterization could not be satisfactorily carried out. In this section, we describe the results of the synthesis and characterization of through-space-conjugated polymers containing [2.2]paracyclophane in the main chain.[5,10]

We synthesized a poly(*p*-aryleneethynylene)-conjugated polymer **3** containing a repeating [2.2]paracyclophane unit in the main chain by the Sonogashira–Hagihara coupling reaction of pseudo-*p*-dibromo[2.2]paracyclophane (**1**) with diethynylbenzene **2**,[10a] as shown in Scheme 1. The polymerization product was obtained in better yield by carrying out the same reaction using the monomers pseudo-*p*-diethynyl[2.2]paracyclophane (**4**) and diiodobenzene **5**; in this case, polymer **3** was obtained in 95% yield with a number-average molecular weight (M_n) of 14500 and polydispersity index (PDI) of 2.4 (Scheme 1). Further, we carried out Mizoroki–Heck coupling of pseudo-*p*-divinyl[2.2]paracyclophane (**6**) with diiodofluorene **7** (Scheme 2) and Suzuki–Miyaura coupling of **1** with fluorenediboronic acid ester **9** (Scheme 3) to obtain corresponding poly(*p*-arylenevinylene)-conjugated polymer **8**[10b] and poly(*p*-arylene)-conjugated polymer **10**,[10c] respectively, in high yields. Thus, we exploited palladium-catalyzed coupling reaction of [2.2]paracyclophane monomers and obtained a variety of [2.2]paracyclophane-containing conjugated polymers **11**–**17**,[10d–10j] which are shown in Chart 1. [2.2]Paracyclophane-containing conjugated polymers **19**–**21** synthesized by oxidative coupling reaction of alkynes (Scheme 4),[11a] polycondensation reaction of silylchloride with acetylide (Scheme 5),[11b] and cycloaddition polymerization of aldothioketenes (Scheme 6),[11c] respectively.



11[10d]
$M_n = 26400$, PDI = 2.5

12[10e]
$M_n = 4400$, PDI = 1.9

13[10f]
$M_n = 4300$, PDI = 3.1

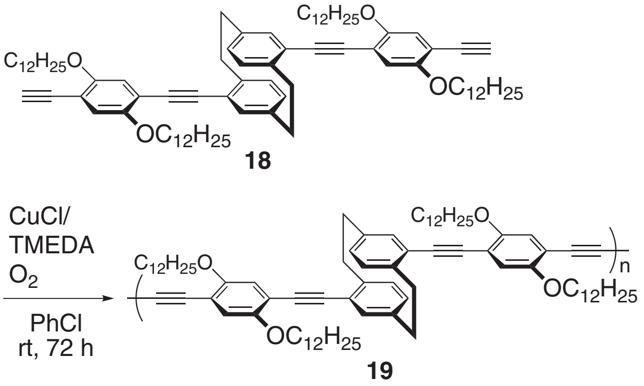
14[10g]
$M_n = 29700$, PDI = 2.6

15[10h]
$M_n = 24500$, PDI = 2.7

16[10i]
$M_n = 4200$, PDI = 2.0

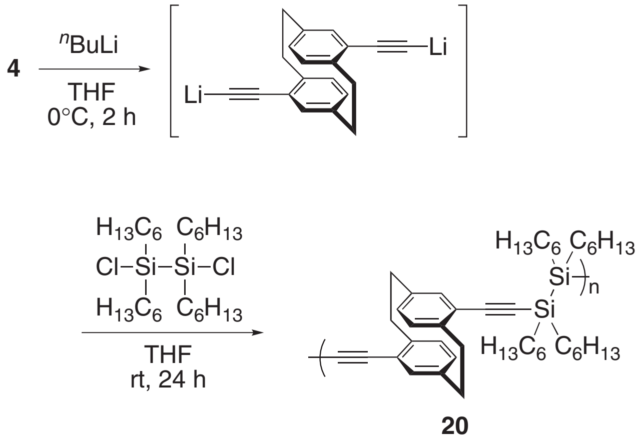
17[10j]
$M_n = 3800$, PDI = 1.3

Chart 1.



19
$M_n = 63000$, PDI = 1.6

Scheme 4.



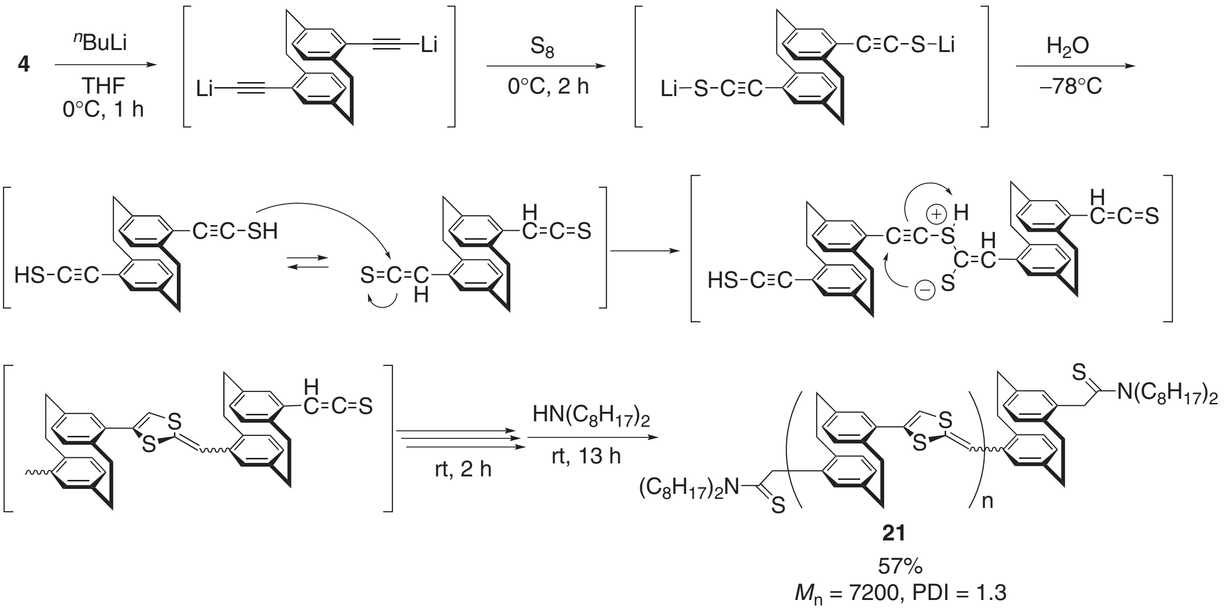
20
$M_n = 10700$, PDI = 1.6

Scheme 5.

All the prepared polymers were soluble in common organic solvents such as THF, $CHCl_3$, CH_2Cl_2, and toluene; this solubility of the polymers enables the characterization of their solutions by NMR, UV–vis absorption, and fluorescence spectroscopy. In addition, they exhibited sufficiently high film-forming ability, when the films were prepared by cast and spin-coating methods. They also exhibited good thermal stability; for example, polymer **10** was found to have a 10% weight loss temperature of approximately 430 °C, as determined by thermogravimetric analysis (TGA) (Figure 1).[10c]

Figures 2A and 2B show the UV–vis absorption and photoluminescence spectra, respectively, of polymer **3** as a representative polymer and its model compound **22** (Chart 2) in dilute $CHCl_3$ solutions. In Figure 2A, the spectra of both the compounds exhibited the typical π–π^* band of a phenylene–ethynylene skeleton. The absorption maximum and absorption edge of polymer **3** were observed at $\lambda_{max} = 387$ and around 440 nm, which were red-shifted compared to those of compound **22**. These results suggest that the [2.2]paracyclophane-containing conjugated polymer exhibited an extension of the π-conjugation length via not only the through-bond conjugation of sp- and sp^2-carbon frameworks but also the through-space interaction of π–π stacking between the benzene rings in the [2.2]paracyclophane units. However, the through-bond conjugation contributes more to the extension of the conjugation length than the through-space conjugation.

Fluorescence spectrum of polymer **3** in dilute $CHCl_3$ exhibited a red-shift of approximately 20 nm compared to the



Scheme 6.

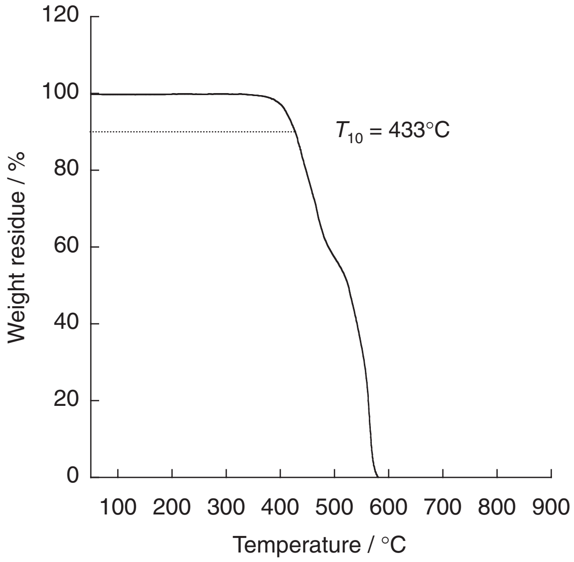


Figure 1. Thermogravimetric analysis (TGA) of polymer **10** under air (10 °C min^{-1}).

spectrum of compound **22**, as shown in Figure 2B. In addition, both polymer **3** and compound **22** emitted bright blue light, and their fluorescence quantum efficiencies were found to be 0.82 and 0.86, respectively.[10j] It is worth noting that the fluorescence spectrum of polymer **3** showed the presence of a clear vibration mode. Namely, polymer **3** did not exhibit excimer-like emission despite the stacked structure of compound **22**. It is known that the emission mechanism of cyclophane compounds can be of two types depending on the conjugation length of one of the two π-systems facing each other and the type of overlap between them.[12] In cyclophane compounds that have fully conjugated and partially overlapping π-systems, the emission occurs from the excited π-systems (emission from "the monomer (chromophore) state"). On the other hand, in the cyclophane compounds that have poorly conjugated π-systems or perfectly overlapping π-systems, excimer emission occurs from the parallel π-systems (emission from "the phane state"). The emissions of polymer **3** were observed at $\lambda_{\max} = 407$ and 430 nm with the appearance of a vibrational structure, which are close to the emissions observed at $\lambda_{\max} = 391$ and 415 nm in the case of compound **22** (Figure 2B). This emission behavior of the cyclophane-containing polymer **3** implies that the emission is from monomer state rather than the phane state (Figure 3).

We recently synthesized through-space-conjugated polymer **17** comprising pseudo-ortho-linked [2.2]paracyclophane units by Sonogashira coupling reaction.[10j] The folded structure of the pseudo-ortho-linked [2.2]paracyclophane monomer prevents the polymerization from proceeding smoothly, and thus polymer **17** was obtained with a low M_n of 3800 and PDI of 1.3. The optical profiles of polymer **17** were similar to those of polymer **3**, which consisted of the pseudo-para-linked [2.2]paracyclophane; these properties were found to depend on the optical properties of the skeleton unit, i.e., the model compound **22**. Synthesis of optically active through-space-conjugated polymers with planar-chiral pseudo-ortho-linked [2.2]paracyclophane units is currently in progress.

The electroluminescent (EL) properties of polymer **8** were examined by fabricating an EL device with a structure represented as ITO/PEDOT–PSS/**8**/BCP/Alq/LiF/Al (ITO = indium–tin oxide, PEDOT = poly(3,4-ethylenedioxythiophene), PSS = poly(4-styrenesulfonic acid), and BCP = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline).[10b] The EL spectrum showed a maximum peak at 490 nm with a turn-on voltage of 13 V. The luminescence brightness was 150 cd m^{-2} at a drive voltage of 19 V and a current density of 546 A m^{-2}. The external quantum efficiency was estimated to be 0.88% at 38 cd m^{-2} under a bias of 14 V. Thus, we showed that a [2.2]paracyclophane-containing through-space-conjugated polymer can be used in the fabrication of optoelectronic devices.

3. Synthesis of [2.2]Paracyclophane-Stacked Dendrimers and Polymers

We demonstrated the synthesis of third- and fourth-generation polyamidoamine (PAMAM) dendrimers **26** and **27** containing [2.2]paracyclophane units on their surface (Scheme 7);[13] this synthesis was the first of its kind. The complete incorporation of [2.2]paracyclophane units in the dendrimers was verified by UV titration experiments; this titration confirmed the formation of the charge-transfer (CT) complex between the cyclophane units on the dendrimer surface and 7,7,8,8-tetracyanoquinodimethane (TCNQ), as shown in Figure 4. The association constant (K_{CT}) of the CT complex formation was determined by using the Benesi–Hildebrand equation and found to be $K_{CT} = 14.7$ ($L\,mol^{-1}$). As shown in Figure 5, the intensity of emissions of [2.2]paracyclophane from 400 to 500 nm increased with an increase in the generation number of the dendrimers, which indicates the intensity of emission from π–π interaction among [2.2]paracyclophane units in the excited state accompanying the increase of the generation number of dendrimers.

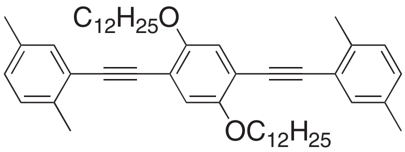


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Chart 2.

On the other hand, polymethylene is a polymer possessing a substituent attached to each carbon atom in the main chain,[14] and polyethylene synthesized by vinyl polymerization has a substituent attached to alternate carbon atoms, as shown in

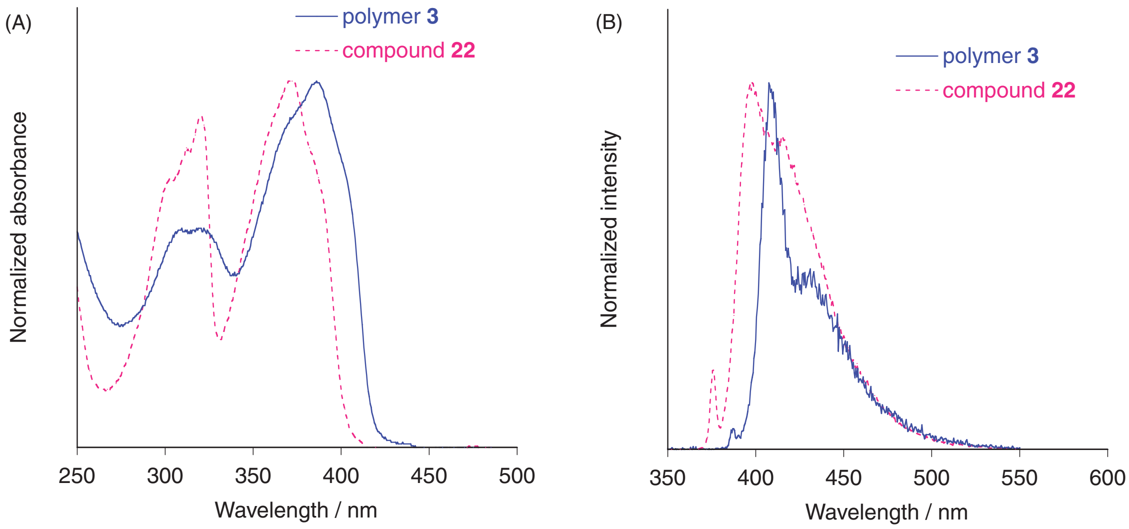


Figure 2. (A) UV–vis absorption spectra of polymer **3** and compound **22** ($CHCl_3$, 1.0×10^{-5} M); (B) fluorescence emission spectra of polymer **3** and compound **22** ($CHCl_3$, 1.0×10^{-5} M).

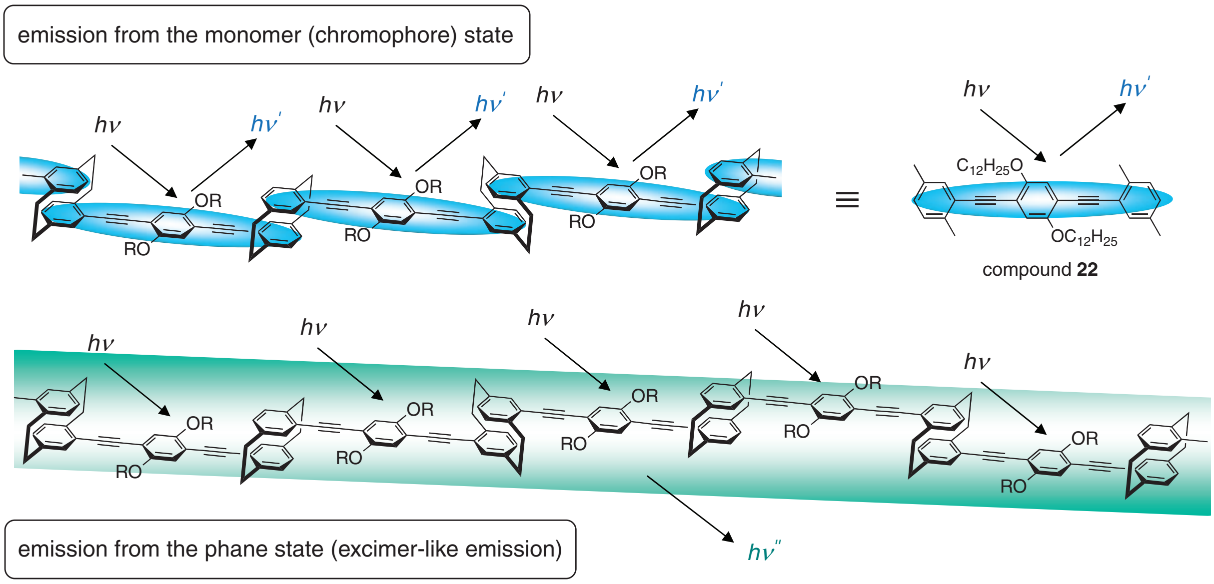
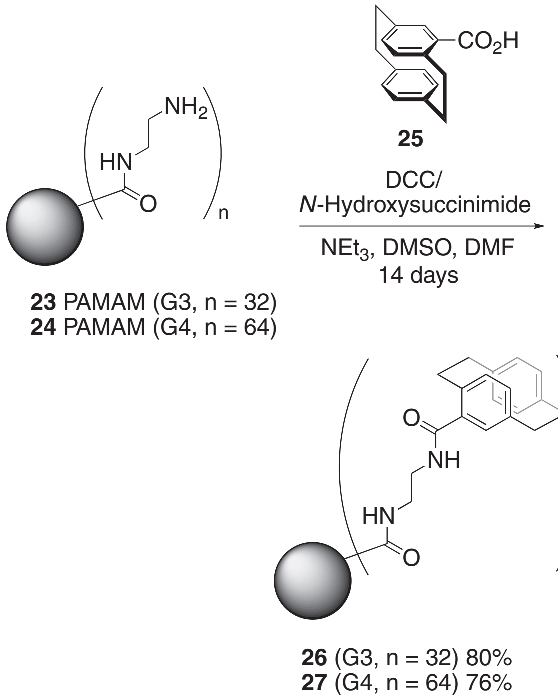


Figure 3. Possible emission mechanism of the cyclophane-containing polymers.



Scheme 7.

Chart 4. Functional groups in the polymethylene chain are closely packed. It is expected that the introduction of bulky [2.2]paracyclophane into a polymethylene backbone as a pendent group provides a π-stacked structure; however, polymethylene has not yet been employed for the scaffold dangling [2.2]paracyclophanes.

As shown in Figure 6, polymethylene **30** was synthesized in 20% yield with M_n of 1100 and PDI of 1.6 by the polymerization of 4-diazomethyl[2.2]paracyclophane (**29**) in the presence of a catalytic amount (2 mol %) of $BF_3 \cdot Et_2O$.[14d,15] Figure 6 includes the matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrum of polymer **30**, which exhibits a major series of peaks regularly separated by the molar mass of a repeating unit (m/z 220). Figure 7 shows the UV–vis absorption spectra of [2.2]paracyclophane, polyethylene analog, and polymer **30** in dilute $CHCl_3$ solution. The absorption maxima of polymer **30** exhibited a remarkable bathochromic shift in comparison with those of [2.2]paracyclophane and polyethylene, which suggests π–π interactions among the [2.2]paracyclophane units in the ground state due to their closely packed structure.

It is well-known that the monosubstituted [2.2]paracyclophane has planar chirality.[8c,16] We successfully synthesized chiral 4-diazomethyl[2.2]paracyclophane monomers (R_p)-**29** and (S_p)-**29** and used them to obtain optically active polymethylenes (R_p)-**30** and (S_p)-**30**, respectively, as shown in Scheme 8.[15] In the CD spectra (Figure 8), they exhibited an intense and mirror-image Cotton effect in $CHCl_3$ solution, while the optically inactive polymer **30** did not exhibit any peaks as expected. According to their patterns of the Cotton effect,[17] optically active polymers (R_p)-**30** and (S_p)-**30** have the possibility to adopt the optically active higher-ordered structure of the polymethylene chain.[15]

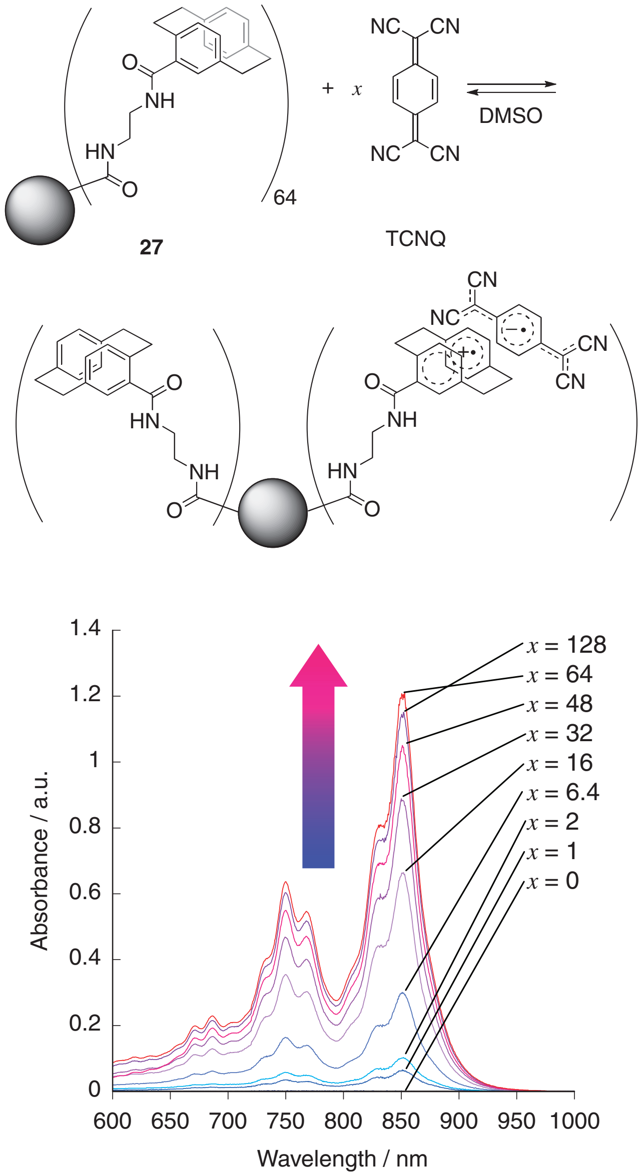


Figure 4. Scheme of the CT complex formation of G4-dendrimer **27** with TCNQ, and UV–vis absorption spectra of CT complexes of G4-dendrimer **27** with TCNQ (absorption of the typical anion radical of TCNQ) in DMSO ([2.2]paracyclophane unit = 2.2×10^{-3} M).

4. Synthesis of [2.2]Paracyclophane-Based Aromatic-Ring-Layered Polymers

Aromatic-ring-layered polymers comprising two parallel aromatic rings on top of each other are expected to be used in the fabrication of single molecular wires and other molecular devices, which exhibit efficient energy and charge transfers through the layered aromatic rings. Recently, we successfully synthesized aromatic-ring-layered polymers consisting of several face-to-face benzene rings, where [2.2]paracyclophane units were the layered aromatic rings on a xanthene skeleton.[18] The key point is that the rotary motion of the two aromatic rings attached at the 4,5-positions of the xanthene skeleton is restricted due to steric hindrance.

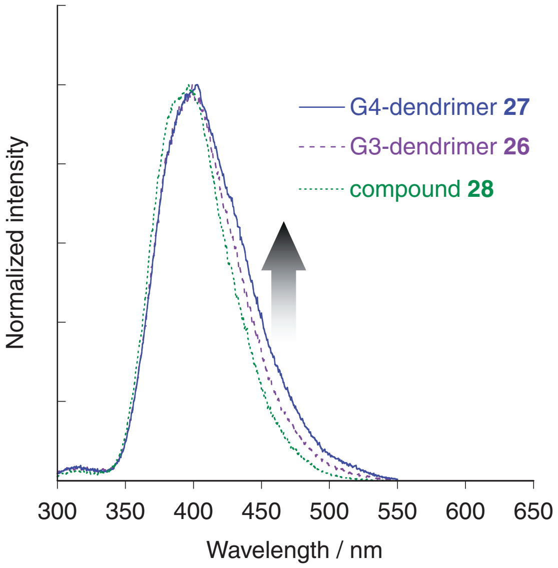


Figure 5. Fluorescence emission spectra of dendrimers **26** (- - -) and **27** (—), and compound **28** (Chart 3) (···) in CH_3OH excited at 225 nm.

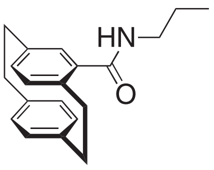


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Chart 3.

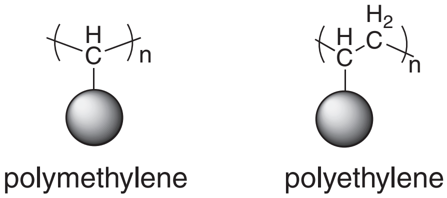


Chart 4.

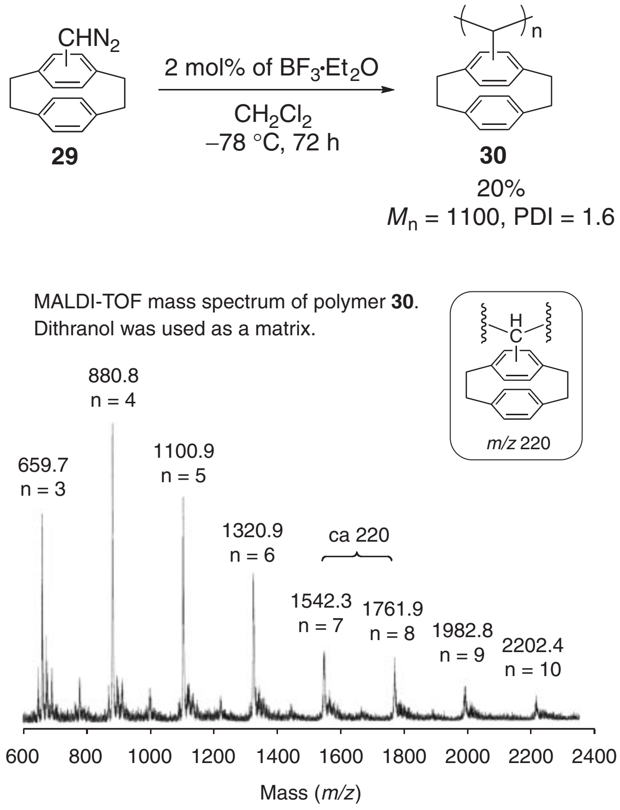


Figure 6. Synthesis of polymer **30**, and its matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrum. Dithranol was used as a matrix.

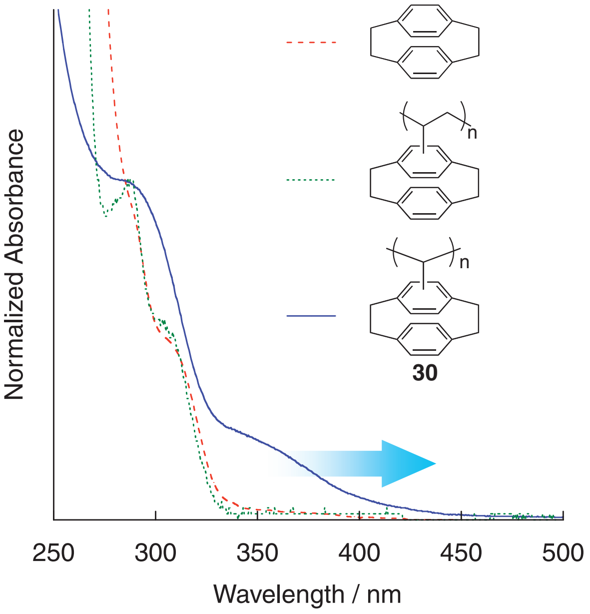
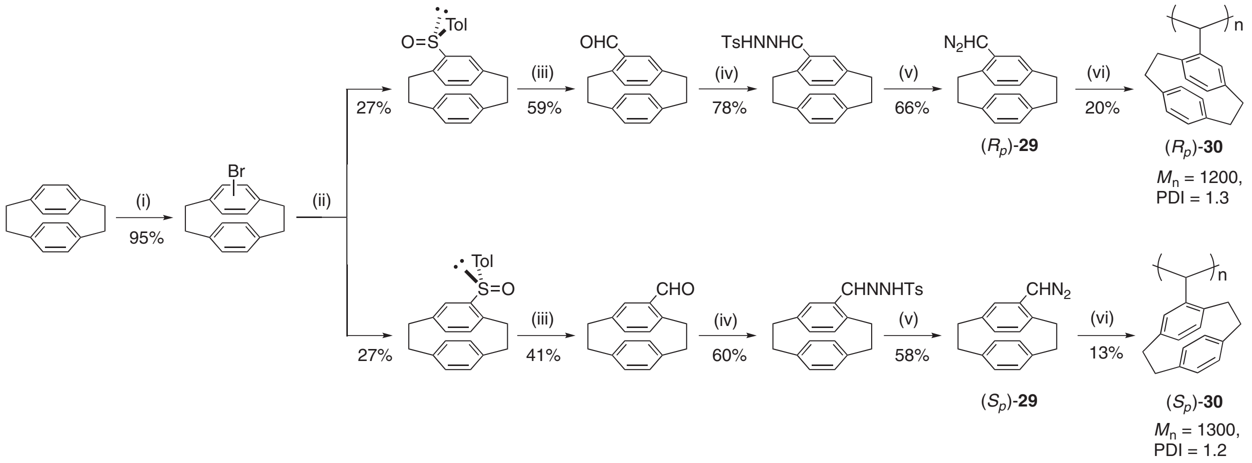


Figure 7. UV–vis absorption spectra of [2.2]paracyclophane, polyethylene, and polymer **30** ($CHCl_3$, 90–200 µM/repeating unit of the polymer).

As shown in Scheme 9, pseudo-*p*-diethynyl[2.2]paracyclophane (**4**), which serves as the layered aromatic ring, 2,7-di-*tert*-butyl-4,5-diiodo-9,9-dimethylxanthene (**31**), which serves as the scaffold, and terminal alkynes **32–35**, which were used as end-capping groups, were polymerized by the Sonogashira–Hagihara coupling reaction. The molecular weights of the resultant polymers **36–39** could be controlled by changing the feed ratio (*x*:*y*:*z*) of the monomers; the polymerization results using different feed ratios are summarized in Table 1. For example, M_n of polymer **36a**, which was obtained in Run 1 (x:y:z = 9:10:2) was evaluated to be 4100 from the ^{1}H NMR integral ratio.[18b] From this result, it can be concluded that in polymer **36a** an average of eight [2.2]paracyclophane units, in other words, sixteen benzenes, are stacked in the polymer main chain.

Figure 9 shows the UV–vis absorption spectra of polymers **36a–36c** and compound **40** (Chart 5) in $CHCl_3$ (1.0×10^{-5} M).[18b] Their absorption spectra exhibited absorption peaks at around 290 and 330 nm characteristic of π–π^* transitions and absorption edges at around 375 nm; these peaks and edges were observed at longer wavelengths than those observed in the case of compound **40**. The spectral features of the absorption



Scheme 8. Reaction conditions: (i) Br_2/Fe in CH_2Cl_2 at rt for 24 h; (ii) 1) *n*-BuLi in THF at −78 °C for 2 h, 2) (*S*)-(−)-menthyl *p*-toluenesulfinate for 12 h; (iii) 1) *t*-BuLi in THF at −78 °C for 3 min, 2) DMF for 12 h; (iv) *p*-toluenesulfonohydrazide in EtOH at 50 °C for 12 h; (v) NaOH in benene/H_2O with benzyltriethylammonium chloride at 65 °C for 2 h; (vi) 2 mol % of $BF_3 \cdot Et_2O$.

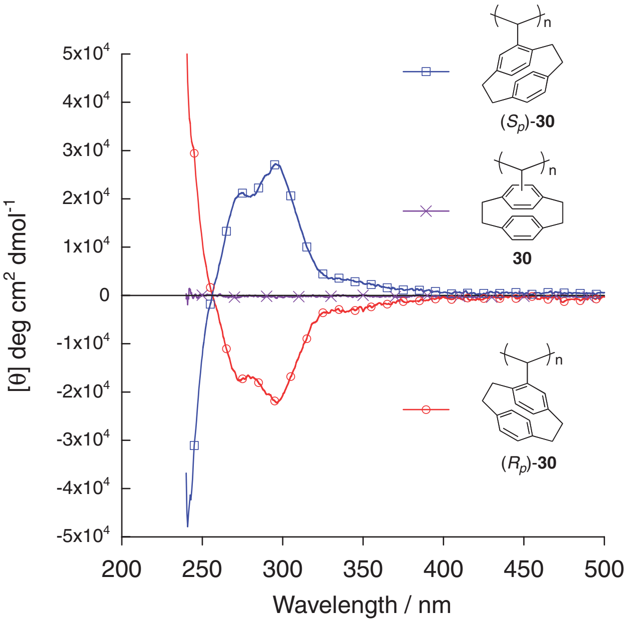


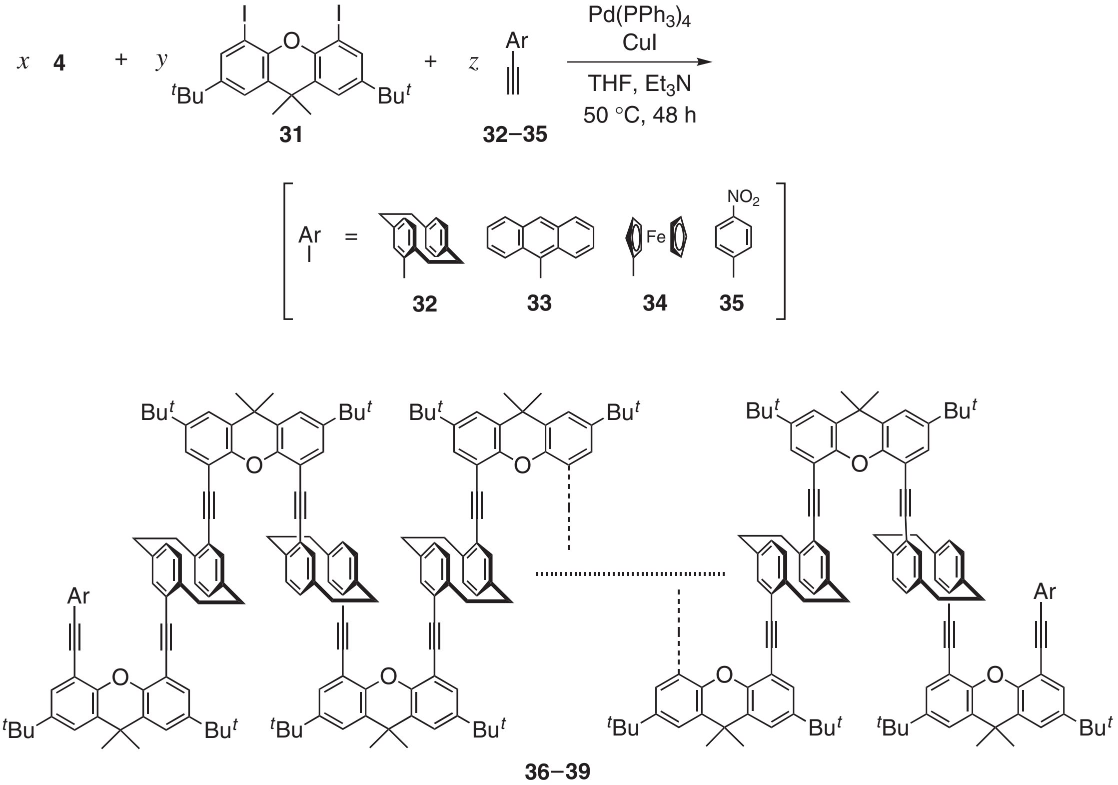
Figure 8. Circular dichroism (CD) spectra of polymers (*R*$_p$)-**30**, (*S*$_p$)-**30**, and **30** ($CHCl_3$, 60–90 µM/repeating unit of the polymer).

spectra of polymers **36a–36c** were independent of the number of layered [2.2]paracyclophane units. It was believed that even polymer **36c** with $M_n = 2100$ (nine benzene rings) exhibited sufficiently extended conjugation via through-space interactions in the ground state. The fluorescence emission spectrum of **36a** in a dilute $CHCl_3$ solution (5.0×10^{-7} M) is also shown in Figure 9. Emission from the layered [2.2]paracyclophane was observed at around 400 nm under the 334 nm excitation.

In order to investigate the structural aspect of the aromatic-ring-layered polymers, we carried out X-ray crystallographic studies of the corresponding model compounds **41** and **42** (Chart 6), which comprised ferrocenes on a xanthene skeleton.[18c] As shown in Figure 10, the ferrocenes and the xanthene units in compound **41** have a twisted conformation, and the dihedral angles between cyclopentadienyl rings and xanthene were 86.4 and 60.9° (top view in Figure 10). The two cyclopentadienyl rings were located in parallel and facing each other. The shortest distance between the intramolecular ferrocenes was 3.491 Å, while the distance between the 4- and 5-positions of xanthene was 4.561 Å (side view in Figure 10). The distance 3.491 Å is almost equal to the sum of the van der Waals radius of an sp^2 carbon (3.40 Å).

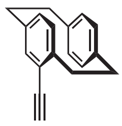
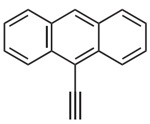
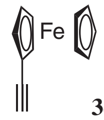
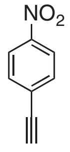
The structure of compound **42** was also successfully elucidated by X-ray crystallographic studies, as shown in Figure 11. The two ferrocenes in compound **42** were twisted in a manner similar to that observed in compound **41**, and the torsion angle between the cyclopentadienyl rings and xanthene was 88.8°. Interestingly, it was found that a benzene ring of a [2.2]paracyclophane unit and xanthene lie on the same plane with a torsion angle of 166.0° despite the steric hindrance. This implies that [2.2]paracyclophane preferably orients itself in π-conjugation with xanthene rings. To avoid steric repulsion between two ferrocenes, the acetylene unit deviates from linearity with C≡C–Ar bond angles of 159.0 and 173.6° (Figure 11). Complete rotation of [2.2]paracyclophane in the polymer main chain is expected to be difficult due to the bulkiness of the [2.2]paracyclophane unit and the offset rotation axis of the pseudo-*p*-diethynyl[2.2]paracyclophane unit. It is clear that the aromatic-ring-layered polymers with xanthene skeleton have sufficient free space, which allows the [2.2]paracyclophane units to twist within the polymer backbone.

Polymer **37b** ($M_n = 4200$) end-capped with two anthracenes exhibited a strong absorption peak at around 270 nm and a broad absorption peak at around 400 nm in addition to the characteristic π–π^* absorption band of [2.2]paracyclophane, as shown in Figure 12.[18b] On comparing the spectrum of **37b** with the absorption spectrum of 9-ethynylanthracene (**33**), it is suggested that the absorption peaks at both 270 and 400 nm are attributed to the end-capping anthracene units. Figure 12 also shows the fluorescence emission spectrum of **37b** in a dilute $CHCl_3$ solution (1.0×10^{-7} M) at an excitation of 334 nm. At this excitation wavelength, only the layered [2.2]paracyclo-



Scheme 9.

Table 1. Results of Polymerization

Run	Terminal alkynes	Feed ratio *x*:*y*:*z*	Polymer	Yield/%	M_n (calcd.)	M_n (^{1}H NMR)
1	 **32**	9:10:2	**36a**	79	5956	4100
2		4:5:2	**36b**	65	3082	3100
3		2:3:1	**36c**	50	1933	2100
4	 **33**	9:10:2	**37a**	70	5896	7500
5		4:5:2	**37b**	50	3022	4200
6		2:3:1	**37c**	65	1872	2600
7	 **34**	9:10:2	**38a**	96	5912	9000
8		4:5:2	**38b**	96	3038	4900
9		2:3:1	**38c**	89	1888	2750
10	 **35**	9:10:2	**39a**	76	5786	5750
11		4:5:2	**39b**	59	2912	3000
12		2:3:1	**39c**	56	1762	1700

phane units are effectively excited, because the end-capping anthracene units do not have an absorption band at around 334 nm. In the fluorescence spectrum (Figure 12), a strong emission peak was observed with the appearance of vibrational structure at around 430 nm, which was attributed to the terminal anthracene units, and a weak emission peak was observed at around 400 nm, which was attributed to the layered [2.2]paracyclophane units.

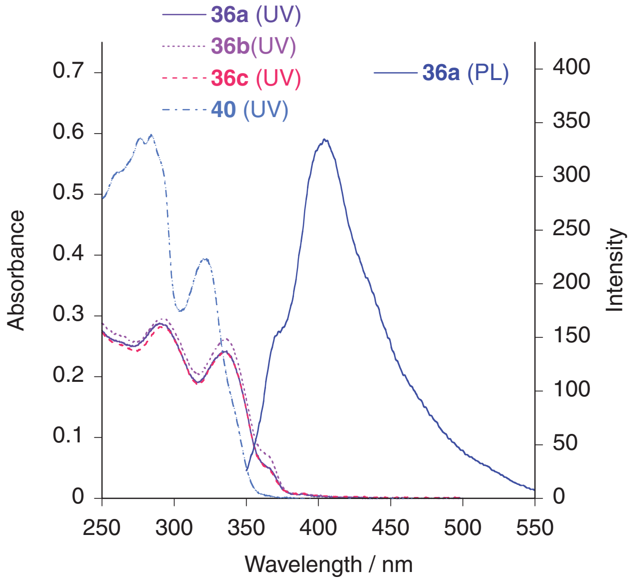
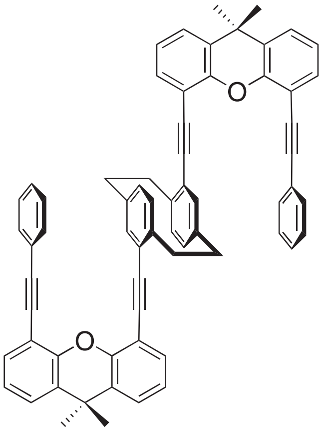
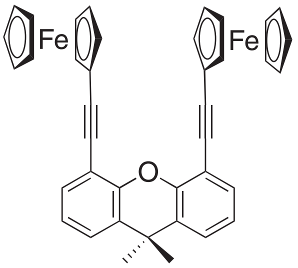


Figure 9. UV–vis absorption spectra of polymers **36a**–**36c** and compound **40** (1.0×10^{-5} M) and fluorescence emission spectrum of polymer **36a** (5.0×10^{-7} M) in $CHCl_3$.

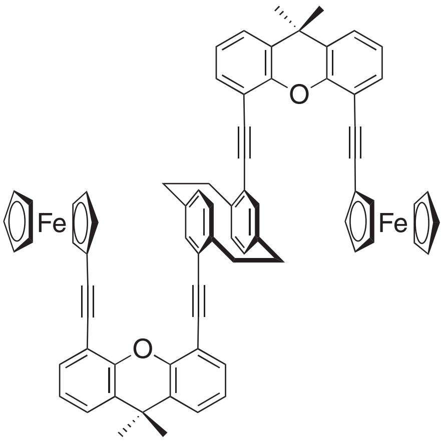


40

Chart 5.



41



42

Chart 6.

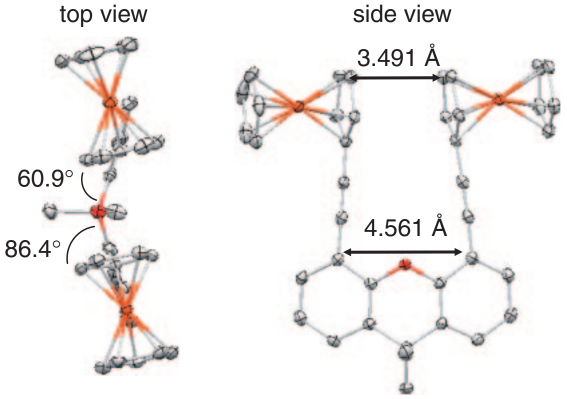


Figure 10. ORTEP drawing of compound **41**; top and side views are shown. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

According to the time-resolved fluorescence spectra of polymer **37b** (Figure 13), we confirmed that as the emission from cyclophane units decreased, the emission from anthracene units increased. From Figures 9 and 12, good overlap between the emission peak of the layered-cyclophane units (at 400 nm in Figure 9) and the absorption peak of 9-ethynylanthracene moieties (at around 400 nm in Figure 12) is observed. These results indicate the occurrence of fluorescence resonance energy transfer (FRET)[19] from the cyclophane units to the end-capping anthracenes. The efficiency of energy transfer from the layered cyclophane units to anthracene units was estimated to be 57% in the case of **37b**. In addition, [2.2]paracyclophane-layered polymers **38a**–**38c** and **39a**–**39c**, which were end-capped with ferrocene and nitrobenzene, respectively, were synthesized (Scheme 9 and Table 1); ferrocene and nitrobenzene act as fluorescence quenchers in these polymers. Fluorescence emissions of the layered [2.2]paracyclophane units in **38a**–**38c** and **39a**–**39c** were effectively quenched due to the energy transfer between them and the terminal fluorescence-quenching moieties.[18c]

By the use of the synthetic approach proposed in our study, it is possible to incorporate various layered aromatic ring structures in a single polymer chain. We believe that polymers containing such layered aromatic rings can be used in the fabrication of single molecular wires exhibiting π–π stacking, and other optoelectronic devices. Currently, we are carrying out further studies on the design and synthesis of aromatic ring layered oligomers and polymers to develop systems that allow unidirectional flow of energy or electrons.

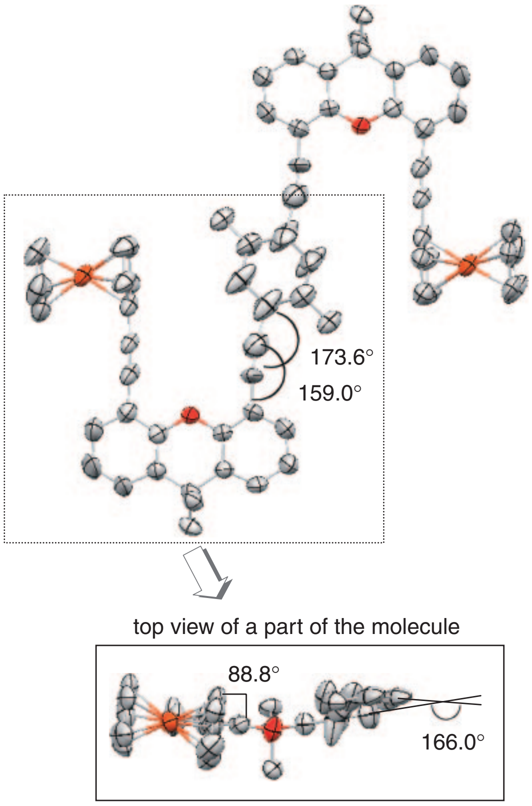


Figure 11. ORTEP drawing of compound **42** including the top view of a part of the molecule. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and solvent (CH_2Cl_2) are omitted for clarity.

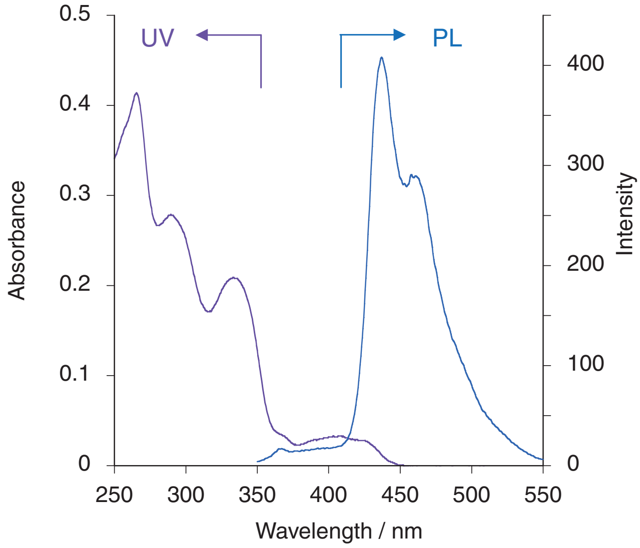


Figure 12. UV–vis absorption spectrum ($CHCl_3$, 1.0×10^{-5} M) and fluorescence spectrum ($CHCl_3$, 1.0×10^{-7} M, excited at 334 nm) of polymer **37b**.

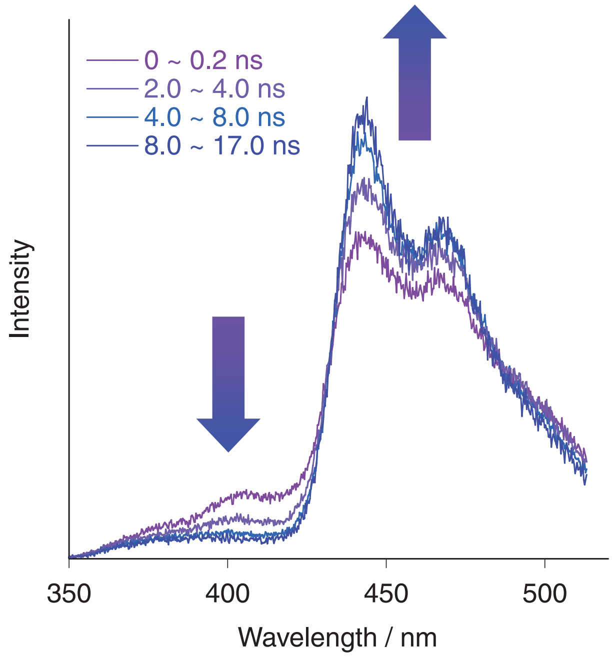


Figure 13. Time-resolved fluorescence spectra of polymer **37a** excited at 337 nm (N_2 laser; with 5 ps temporal resolution using 2D photon counting method) in $CHCl_3$.

5. Conclusion

We have demonstrated the successful incorporation of [2.2]paracyclophane units into conjugated polymer backbones and developed corresponding through-space-conjugated polymers and aromatic-ring-layered polymers. We also synthesized [2.2]paracyclophane-containing PAMAM dendrimers and optically active polymethylenes. These polymers and dendrimers are the first well-defined and well-characterized conjugated polymers with cyclophane units in their main chain. We studied the properties of the [2.2]paracyclophane-containing through-space-conjugated polymers and elucidated the role of the [2.2]paracyclophane unit in the polymer. We demonstrated the use of these through-space-conjugated polymers in the opto-electronic devices such as an EL device. Further, we have developed the synthetic scheme for a new π-stacked polymer comprising layered aromatic rings on xanthene skeleton as the scaffold. The occurrence of FRET from the layered cyclophanes to the end-capping aromatic moieties was verified. Thus, our study has demonstrated the possibility of the use of aromatic-ring-layered polymers as single molecular wires. The synthetic strategy used in our study allows the construction of π-stacked structures using various aromatic compounds, which can be used in the fabrication of novel single molecular wires and unique optoelectronic devices.

References

1 a) *Science and Applications of Conducting Polymers*, ed. by W. R. Salaneck, D. T. Clark, E. J. Samuelsen, Adam Hilger, Bristol, **1991**. b) *Handbook of Organic Conductive Molecules*, ed. by H. S. Nalwa, Wiley, Chichester, **1997**. c) *Handbook of Conducting Polymers*, 3rd ed., ed. by T. A. Skotheim, R. L. Elsenbaumer, J. R. Reynolds, Marcel Dekker, New York, **2006**.

2 a) H. Shirakawa, *Angew. Chem., Int. Ed.* **2001**, *40*, 2574. b) A. G. MacDiarmid, *Angew. Chem., Int. Ed.* **2001**, *40*, 2581. c) A. J. Heeger, *Angew. Chem., Int. Ed.* **2001**, *40*, 2591.

3 a) *Modern Acetylene Chemistry*, ed. by P. J. Stang, F. Diederich, VCH, Weinheim, **1995**. b) *Acetylene Chemistry*, ed. by

F. Diederich, P. J. Stang, R. R. Tykwinski, Wiley-VCH, Weinheim, **2005**.

4 a) D. T. Glatzhofer, D. T. Longone, *J. Polym. Sci., Part A: Polym. Chem.* **1986**, *24*, 947. b) D. T. Longone, D. T. Glatzhofer, *J. Polym. Sci., Part A: Polym. Chem.* **1986**, *24*, 1725. c) J. Ulański, J. Sielski, D. T. Glatzhofer, M. Kryszewski, *J. Phys. D: Appl. Phys.* **1990**, *23*, 75. d) J. Ulański, J. Kubacki, I. Głowacki, M. Kryszewski, D. T. Glatzhofer, *J. Appl. Polym. Sci.* **1992**, *44*, 2103. e) D. J. Guerrero, D. T. Glatzhofer, *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 457. f) T. Nakano, K. Takewaki, T. Yade, Y. Okamoto, *J. Am. Chem. Soc.* **2001**, *123*, 9182. g) T. Nakano, T. Yade, *J. Am. Chem. Soc.* **2003**, *125*, 15474. h) T. Nakano, T. Yade, M. Yokoyama, N. Nagayama, *Chem. Lett.* **2004**, *33*, 296. i) T. Nakano, T. Yade, Y. Fukuda, T. Yamaguchi, S. Okumura, *Macromolecules* **2005**, *38*, 8140. j) T. Yade, T. Nakano, *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 561. k) T. Nakano, T. Yade, *Chem. Lett.* **2008**, *37*, 258. l) S. A. Jenekhe, M. M. Alam, Y. Zhu, S. Jiang, A. V. Shevade, *Adv. Mater.* **2007**, *19*, 536. m) A. García Martínez, J. Osío Barcina, A. de Fresno Cerezo, A.-D. Schlüter, J. Frahn, *Adv. Mater.* **1999**, *11*, 27.

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

6 a) Y. Morisaki, T. Ishida, Y. Chujo, *C. R. Chim.* **2009**, *12*, 332. b) Y. Morisaki, T. Ishida, Y. Chujo, *Polym. J.* **2003**, *35*, 501. c) Y. Morisaki, T. Ishida, Y. Chujo, *Org. Lett.* **2006**, *8*, 1029. d) Y. Morisaki, T. Ishida, Y. Chujo, *Polym. Bull.* **2006**, *57*, 623.

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

8 a) D. J. Cram, N. L. Allinger, *J. Am. Chem. Soc.* **1955**, *77*, 6289. b) F. Vöctle, *Cyclophane Chemistry: Synthesis, Structures and Reactions*, John Wiley & Sons, Chichester, **1993**. c) V. Rozenberg, E. Sergeeva, H. Hopf, in *Modern Cyclophane Chemistry*, ed. by R. Gleiter, H. Hopf, Wiley-VCH, Weinheim, Germany, **2004**. Recent review, see: d) H. Hopf, *Angew. Chem., Int. Ed.* **2008**, *47*, 9808.

9 a) L. Guyard, P. Audebert, *Electrochem. Commun.* **2001**, *3*, 164. And also, see: 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.

10 a) Y. Morisaki, Y. Chujo, *Macromolecules* **2002**, *35*, 587. b) Y. Morisaki, Y. Chujo, *Macromolecules* **2004**, *37*, 4099. c) Y. Morisaki, Y. Chujo, *Bull. Chem. Soc. Jpn.* **2005**, *78*, 288. d) Y. Morisaki, Y. Chujo, *Chem. Lett.* **2002**, 194. e) Y. Morisaki, N. Wada, Y. Chujo, *Polym. Bull.* **2005**, *53*, 73. f) Y. Morisaki, N. Wada, Y. Chujo, *Polymer* **2005**, *46*, 5884. g) Y. Morisaki, T. Ishida, H. Tanaka, Y. Chujo, *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 5891. h) Y. Morisaki, Y. Chujo, *Macromolecules* **2003**, *36*, 9319. i) Y. Morisaki, T. Ishida, Y. Chujo, *Macromolecules* **2002**, *35*, 7872. j) Y. Morisaki, N. Wada, M. Arita, Y. Chujo, *Polym. Bull.* **2009**, *62*, 305.

11 a) Y. Morisaki, Y. Chujo, *Polym. Bull.* **2002**, *49*, 209. b) Y. Morisaki, F. Fujimura, Y. Chujo, *Organometallics* **2003**, *22*, 3553. c) Y. Morisaki, L. Lin, Y. Chujo, *Polym. Bull.* **2009**, *62*, 737.

12 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.

13 Y. Morisaki, Y. Shiotani, L. Lin, Y. Chujo, *Polym. J.* **2008**, *40*, 779.

14 Polymethyelnes were synthesized by several methods. For example, Lewis acid-catalyzed polymerization of diazoalkanes, see: a) H. Meerwein, *Angew. Chem.* **1948**, *60*, 78. b) S. W. Kantor, R. C. Osthoff, *J. Am. Chem. Soc.* **1953**, *75*, 931. c) J. Feltzin, A. J. Restaino, R. B. Mesrobian, *J. Am. Chem. Soc.* **1955**, *77*, 206. d) C. E. H. Bawn, A. Ledwith, P. Matthies, *J. Polym. Sci.* **1958**, *33*, 21. e) G. W. Cowell, A. Ledwith, *Q. Rev. Chem. Soc.* **1970**, *24*, 119. f) M. Imoto, T. Nakaya, *J. Macromol. Sci., Part C: Polym. Rev.* **1972**, *7*, 1. g) M. Mucha, B. Wunderlich, *J. Polym. Sci.: Polym. Phys. Ed.* **1974**, *12*, 1993. Pd-catalyzed polymerization of alkyl diazoacetate, see: h) E. Ihara, N. Haida, M. Iio, K. Inoue, *Macromolecules* **2003**, *36*, 36. i) E. Ihara, M. Fujioka, N. Haida, T. Itoh, K. Inoue, *Macromolecules* **2005**, *38*, 2101. j) E. Ihara, A. Nakada, T. Itoh, K. Inoue, *Macromolecules* **2006**, *39*, 6440. k) E. Ihara, M. Kida, M. Fujioka, N. Haida, T. Itoh, K. Inoue, *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 1536. Cu-catalyzed polymerization of alkyl diazoacetate, see: l) L. Liu, Y. Song, H. Li, *Polym. Int.* **2002**, *51*, 1047. Rh-catalyzed polymerization of alkyl diazoacetate, see: m) D. G. H. Hetterscheid, C. Hendriksen, W. I. Dzik, J. M. M. Smits, E. R. H. v. Eck, A. E. Rowan, V. Busico, M. Vacatello, V. V. A. Castelli, A. Segre, E. Jellema, T. G. Bloemberg, B. d. Bruin, *J. Am. Chem. Soc.* **2006**, *128*, 9746. n) A. F. Noels, *Angew. Chem., Int. Ed.* **2007**, *46*, 1208. BH_3-catalyzed polymerization of alkyl diazoacetate, see: o) J. Bai, L. D. Burke, K. J. Shea, *J. Am. Chem. Soc.* **2007**, *129*, 4981.

15 N. Wada, Y. Morisaki, Y. Chujo, *Macromolecules* **2009**, *42*, 1439.

16 Chiral resolution of the precursors was carried out according to the procedure established by Rowlands and co-workers, see: a) P. B. Hitchcock, G. J. Rowlands, R. Parmar, *Chem. Commun.* **2005**, 4219. b) G. J. Rowlands, *Org. Biomol. Chem.* **2008**, *6*, 1527.

17 a) O. E. Weigang, Jr., M. J. Nugent, *J. Am. Chem. Soc.* **1969**, *91*, 4555. b) C. Rosini, R. Ruzziconi, S. Superchi, F. Fringuelli, O. Piermatti, *Tetrahedron: Asymmetry* **1998**, *9*, 55.

18 a) Y. Morisaki, Y. Chujo, *Tetrahedron Lett.* **2005**, *46*, 2533. b) Y. Morisaki, T. Murakami, Y. Chujo, *Macromolecules* **2008**, *41*, 5960. c) Y. Morisaki, T. Murakami, Y. Chujo, *J. Inorg. Organomet. Polym. Mater.* **2009**, *19*, 104. d) Y. Morisaki, T. Murakami, T. Sawamura, Y. Chujo, *Macromolecules* **2009**, *42*, 3656.

19 T. Förster, *Naturwissenschaften* **1946**, *33*, 166.

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