Star-Shaped ROMP Polymers Coated with Oligothiophenes That Exhibit Unique Emission

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ABSTRACT: A series of oligo(thiophene)-modified "soluble" star-shaped ring-opening metathesis polymerization (ROMP) polymers were prepared by sequential living ROMP of norbornene and a cross-linking agent using a molybdenum-alkylidene catalyst, followed by Wittig-type coupling for termination with oligo-(thiophene) carboxaldehydes. The resultant star-shaped ROMP polymers displayed unique emission properties affected by the core size and arm repeat units as well as the kind of oligothiophene coated. The effects of the thiophene groups on photophysical properties of star-shaped/linear polymers were studied *via* time-resolved fluorescence spectroscopy. Fluorescence lifetimes were determined in THF as 400, 640, 730, and 820 ps for **Star 3TPh, Linear 3TPh, Star 4T,** and **Linear 4T,** respectively. A significant enhancement of the nonradiative rate constants k_{nr} in the star-shaped polymers results in relatively lower fluorescence quantum yields and shorter fluorescence lifetimes compared to the corresponding linear polymers.
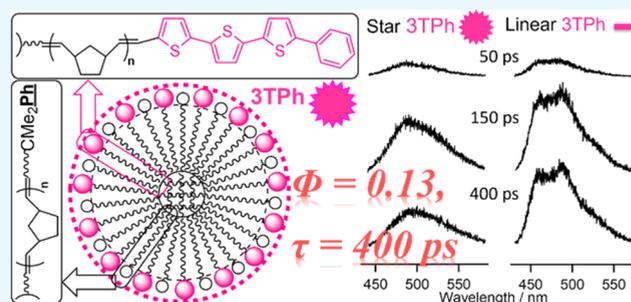
1. INTRODUCTION

The study of star-shaped polymers, as one of the simplest nonlinear polymeric materials consisting of linear arms connected at a central branched core, has been an attractive subject, especially in the field of polymer chemistry and materials science.[1−7] The living polymerization technique (absence of undesirable side reactions such as chain transfer and termination, coupling and/or disproportionation *etc.*) plays an essential key role in the precise synthesis, including the end-modification, different and/or block arms (miktoarm stars).[1−7] Among them, the one-pot synthesis by adopting living ring-opening metathesis polymerization (ROMP),[8−15] conducted by the sequential addition of monomers and cross-linkers (CLs),[12,16−37] attracts considerable attention. Two major approaches (Scheme 1), such as arm- (brush) first approach using a ruthenium-carbene catalyst (so-called third-generation Grubbs catalyst)[17−28] and core-first (in and out) approach using a molybdenum-alkylidene catalyst,[29−35] have been known. Moreover, the preparation of cross-linked ROMP polymers applied as monolith materials that are insoluble in common organic solvents was also reported.[8,9,38−40] It was demonstrated that the latter approach using Mo(CHCMe₂Ph)-(N-2,6-iPr₂C₆H₃)(OtBu)₂ (**Mo cat**) enables us an exclusive synthesis of end-functionalized (surface-modified) star-shaped ROMP polymers[29−35] because the propagating chain end, molybdenum-alkylidene species containing polymer chain, is highly reactive toward aldehyde through Wittig-type coupling.[10,12,41−43] The resultant polymers are size-controlled spherical materials having diameters close to the calculated

values in norbornene (NBE) repeat units through a TEM micrograph (exemplified in Figure 1).[29,30,32]

It has been demonstrated that the resultant star-shaped ROMP polymers by using ruthenium-carbene and molybdenum-alkylidene catalysts can be applied to the materials with better-controlled release/actions,[18,20] magnetic resonance imaging agents,[21,25] and/or degradable materials[28] or supported molecular catalysts[32,35] (by Mo catalyst, Figure 1, bottom; Ti cat.) or unique emitting materials.[31] We demonstrated that oligo(thiophene)-modified (coated) "soluble" star-shaped polymers exhibit unexpected blue emission properties (Figure 1 top). The origin of these unique emission properties could be due to an integration of the ROMP polymers through a space interaction of the oligothiophene moiety with the phenyl group in the initiating fragment. Moreover, the blue emission was turned into a white emission upon the addition of 2-[2-[(E)-4-(dimethylamino)styryl]-6-methyl-4H-pyran-4-ylidene]malononitrile.[31]

Since we recently demonstrated the one-pot synthesis of end-modified star-shaped polymers with more arms by adopting the living ROMP technique using **Mo cat**, as shown in Scheme 2, we have thus prepared a series of

Scheme 1. Two Major Approaches, (a) Arm-First and (b) Core-First Approach in the Synthesis of Star-Shaped Polymers by Adopting Living ROMP of Cyclic Olefins by Mo or Ru Catalysts[a]

[a]CL = cross-linking agent.

oligo(thiophene)-modified star-shaped ROMP polymers with different arm numbers and core size (by modification of CL/Mo molar ratio and addition of NBE in the core formation step, Scheme 2). Through analysis of UV−vis spectra, fluorescence spectra, and time-resolved emission spectral analysis, we explored the reason for the unique emission and factors affecting the optical property.

2. RESULTS AND DISCUSSION

2.1. Synthesis of the Oligo(thiophene)-Coated Star-Shaped ROMP Polymers. According to the established procedure,[29−35] various star-shaped polymers modified with oligo(thiophene) were prepared through the core-first (in and out) approach in the living ROMP (Scheme 2), consisting of 4 key steps by sequential addition of a cross-linker (CL, 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo-endo*-dimethanonaphtalene, *exo/endo* = 0.15:1.00),[44] NBE, and aldehyde for the termination [ArCHO, Ar = 2,2′-bithiophene-5-carboxaldehyde (**2T-CHO**), 2,2′:5′,2″-terthiophene-5-carboxaldehyde (**3T-**

CHO), 5″-(3,4,5-trimethoxyphenyl)-2,2′:5′,2″-terthiophene-5-carboxaldehyde (**MP3T-CHO**),[a] 5″-phenyl-2,2′:5′,2″-terthiophene-5-carboxaldehyde (**3TPh-CHO**),[a] and 2,2′:5′,2″:5″,2‴-quaterthiophene-5-carboxaldehyde (**4T-CHO**)].[31] **Mo cat** has been chosen as the initiator because of its promising ability for the preparation of the multiblock ring-opened copolymers in a precise manner and the ability for the quantitative introduction of functionality into the polymer chain end *via* a Wittig-like reaction (a cleavage of the ROMP polymer−metal double bonds with aldehyde; excess amount for achieving the complete conversion).[12,15,29−35,41−43] These oligothiophenes were chosen because an interaction between terthiophene and the phenyl group in the initiation fragment was assumed through the previous communication,[31] and this should be affected by the thiophene repeat unit and the substituent; this effect was also observed as the end-group effect in poly(fluorene-2,7-vinylene)s on emission properties.[a,45] The selected polymerization results are summarized in Table 1.

Figure 1. End-modified star-shaped polymers containing terthiophene, which show unique emissions [white light emission upon addition of 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4Hpyran, left top], phenoxy substituent for supported molecular catalysts (bottom).

As demonstrated in Table 1, the oligo(thiophene)-coated star-shaped ROMP polymers terminated with various aldehydes (**2T-CHO**, **3T-CHO**, **MP3T-CHO**, **3TPh-CHO**, and **4T-CHO**, sample names, abbreviations of polymers chosen in this study are also shown in Scheme 2) possessed high molecular weights ($M_n = 0.98–2.79 \times 10^5$, prepared by approaches 1 and 2, Scheme 2) and uniform molecular weight distributions ($M_w/M_n = 1.27–1.88$). The resultant polymers were highly soluble in ordinary organic solvents, such as toluene, tetrahydrofuran, chloroform, or dichloromethane. It turned out that, as reported previously,[33−35] an increase in CL ($10 \rightarrow 15$ equiv to Mo) resulted in affording the polymers with large M_n values [e.g. $M_n = 1.14 \times 10^5$ (run 1) vs 1.51×10^5 (run 2); 1.00×10^5 (run 7) vs 1.52×10^5 (run 8)], suggesting the formation of a star-shaped polymer with increased arm numbers (more branching). The cross-linking density of the polymers could be modified by the addition of NBE (with CL) in the core-formation step [2nd reaction, so-called approach 2, Scheme 2, $M_n = 1.51 \times 10^5$ (run 2) vs 1.59×10^5 (run 3)]. As reported previously, the increase in the NBE amount (NBE/Mo moral ratio) in the third step (from 25 to 50 equiv) led to a notable increase in the M_n value [e.g. $M_n = 1.51 \times 10^5$ (run 2) vs 2.36×10^5 (run 4)], clearly suggesting the formation of star-shaped ROMP polymers. The resultant star-shaped polymers with different end-groups (runs 2, 6, 8, 10, 14) possessed similar M_n values ($1.36–1.55 \times 10^5$) with unimodal molecular weight distributions ($M_w/M_n = 1.29–1.54$), which are also close to those of the reported star ROMP polymers terminated with 4-pyridinecarboxaldehyde.[32−34]

2.2. UV−Vis and Fluorescence Spectra of Oligo(thiophene)-Coated Star-Shaped ROMP Polymers. Figure 2 shows UV−vis (1.0×10^{-5} M in THF at 25 °C) and fluorescence spectra (1.0×10^{-6} M in THF at 25 °C) of the oligo(thiophene)-coated star-shaped ROMP polymers, expressed as **Star 2T** ($M_n = 155\,000$, $M_w/M_n = 1.33$, run 6 in Table 1), **Star 3T** ($M_n = 152\,000$, $M_w/M_n = 1.29$, run 8), **Star MP3T** ($M_n = 150\,000$, $M_w/M_n = 1.36$, run 10), **Star 3TPh** ($M_n = 151\,000$, $M_w/M_n = 1.54$, run 2), and **Star 4T** ($M_n = 136\,000$,

$M_w/M_n = 1.41$, run 14). Additional UV−vis and fluorescence spectra are shown in the Supporting Information.

It was revealed that, as shown in Figure 2a, the absorption bands in **Star 3T** ($\lambda_{max} = 388$ nm) and **Star 4T** (409 nm) were shifted to a longer wavelength relative to those in **3T** (354 nm) and **4T** (391 nm, Figure S5, Supporting Information),[31] respectively. As reported previously,[9] the observed redshift in these star-shaped polymers could be explainedas due to the presence of an interaction of oligo(thiophene) with the phenyl group in the initiation fragment.[31] Similar redshifted absorption bands (λ_{max} values) were observed in **Star MP3T** (419 nm), **Star 3TPh** (412 nm), and **Star 4T** (409 nm), suggesting an extension of the conjugation units through the interaction. It should be noted that the λ_{max} value in the absorption in **Star 3T** (388 nm) is redshifted from its **Linear 3T** ($\lambda_{max} = 377$ nm, Figure S2, Supporting Information), and similar redshifts were observed in the case of **Star 2T**, **Star 3TPh**, and **Star MP3T** (Figures S1, S3, and S4, Supporting Information). In contrast, such a trend was not significant between **Star 4T** and **Linear 4T** (Figure S2, Supporting Information) although the reason is not clear at this moment. The observed slight redshift in the λ_{max} value of **Star MP3T** compared to that of **Star 3TPh** (Figure 2a) would be probably attributed to the electron-donating methoxy group that can reduce the HOMO energy level and facilitate the p−π conjugated effect, thereby reducing the energy of the electronic transition. However, a negligible difference in their emission intensities in higher vibronic bands was observed in their fluorescence spectra (Figure 2b).

It was revealed that λ_{max} values in the fluorescence spectra (Figure 2b) of **Star 4T** (479 and 507 nm), **Star MP3T** (480 and 511 nm), and **Star 3TPh** (475 and 505 nm) show a longer wavelength relative to those of **Star 2T** (393 and 413 nm, Figure S6, Supporting Information) and **Star 3T** (443 and 472 nm). The observed redshits correspond to the redshifts in their absorption spectra.

Figure 3 (left column) shows fluorescence spectra (in THF at 25 °C with excitation at 410 nm) of the star ROMP polymers containing the same end group (**3TPh**) prepared with a different NBE length (**Star-3TPh$_{50}$**, run 4, Table 1), amount of CL (**CL$_{10}$-Star-3TPh**, run 1), approach in the core formation (addition of NBE in the core formation, Scheme 1, expressed as **A2-Star-3TPh**, run 3). These spectra were measured in THF with different concentrations (1.0×10^{-5}, 1.0×10^{-6}, and 1.0×10^{-7} M on the basis of **3TPh** fragment estimated on the basis of molar ratio), as demonstrated previously;[31] the intramolecular interaction (within the star, thiophene, and phenyl group in the initiating fragment) should be more significant than the intermolecular interaction (between the stars) under low concentration conditions. These samples were chosen to study the effects of the cross-linking efficiency (amount of CL, core size) and arm number/length on the emission properties.

The fluorescence intensity in a series of star-shaped polymers containing **3TPh** end group (under high concentration conditions, 1.0×10^{-5} M) increased in the order: **Star-3TPh**, **CL$_{10}$-Star-3TPh** < **A2-Star-3TPh** < **Star-3TPh$_{50}$**. In contrast, the intensity under low concentration conditions (1.0×10^{-6} M) increased in the order: **CL$_{10}$-Star-3TPh** ≪ **Star-3TPh**, **A2-Star-3TPh**, **Star-3TPh$_{50}$**. As demonstrated previously,[31] these emissions could be explained as due to the degree of intramolecular and intermolecular interactions between the thiophene group and phenyl group in the

Scheme 2. Synthesis of Oligo(thiophene)-Modified Star-Shaped Polymers by Living ROMP, and Abbreviations of Polymer Samples Employed in This Study
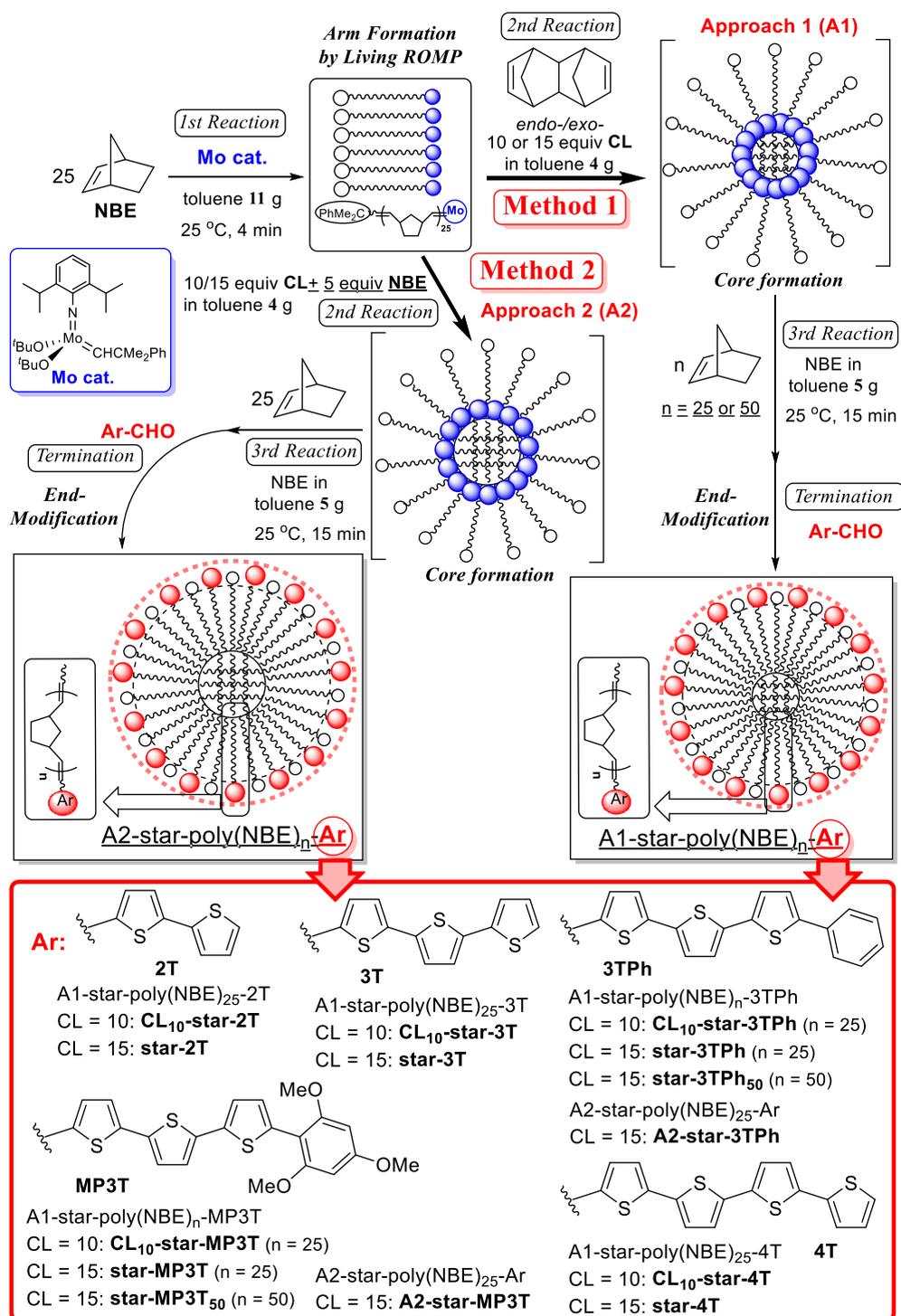
initiation fragment. It was revealed that, in both cases (1.0×10^{-5}, 1.0×10^{-6} M), **A2-Star-3TPh** showed higher fluorescence intensities than those in **Star-3TPh**. Moreover, **Star-3TPh** showed higher intensities than those in **CL$_{10}$-Star-3TPh** under low concentration conditions (1.0×10^{-6} M), whereas a significant difference was not observed under rather high concentration conditions (1.0×10^{-5} M). These clearly suggest that an increase in these interactions (increase in the intensity) could be explained as due to an increase in arm

numbers, which should facilitate the intramolecular interaction (within the star). Moreover, **Star-3TPh$_{50}$** showed higher fluorescence intensity under low concentration conditions (Figure 3 left), but the degree became close to **A2-Star-3TPh** (and **Star-3TPh**, Figure 3 left). Since the NBE arm containing **3TPh** in **Star-3TPh$_{50}$** should be longer than that containing the phenyl group of the initiating fragment, previously confirmed by both TEM and AFM,[29,30,32] as also explained in our previous report (arm length of two fragments, phenyl

Table 1. Synthesis of Star-Shaped Polymers by Living ROMP (Two Approaches, Scheme 2)[a]

run	2nd			3rd		terminator Ar	$M_n{}^c \times 10^{-4}$	$M_w/M_n{}^c$	yield[e]/%	sample name for spectra
	CL^b	NBE^b	time/min	NBE^b	time/min					
1	10	0	50	25	15	3T-Ph	11.4	1.27	85	**CL$_{10}$-Star-3TPh**
2	15	0	50	25	15	3T-Ph	15.1	1.54	91	**Star 3TPh**
3	15	5	50	25	15	3T-Ph	15.9	1.58	85	**A2-Star-3TPh**
4	15	0	50	50	15	3T-Ph	23.6	1.49[d]	80	**Star 3TPh$_{50}$**
5	10	0	50	25	15	2T	11.5	1.15	90	**CL$_{10}$-Star-2T**
6	15	0	50	25	15	2T	15.5	1.33	88	**Star 2T**
7	10	0	50	25	15	3T	10.0	1.24	84	**CL$_{10}$-Star-3T**
8	15	0	50	25	15	3T	15.2	1.29	81	**Star 3T**
9	10	0	50	25	15	MP3T	11.2	1.18	80	**CL$_{10}$-Star-MP3T**
10	15	0	50	25	15	MP3T	15.0	1.36	83	**Star MP3T**
11	15	5	50	25	15	MP3T	15.8	1.88	81	**A2-Star-MP3T**
12	15	0	50	50	15	MP3T	27.9	1.75[d]	73	**Star MP3T$_{50}$**
13	10	0	50	25	15	4T	9.8	1.25	90	**CL$_{10}$-Star-4T**
14	15	0	50	25	15	4T	13.6	1.41	90	**Star 4T**

[a]Conditions: toluene (total 20.0 g) at 25 °C, **Mo cat** 2.00×10^{-5} mol (detailed procedure, see Scheme 2). [b]Molar ratio of NBE/Mo or CL/Mo. [c]GPC data in THF *vs* polystyrene stds. [d]Bimodal molecular weight distribution. [e]Isolated yield (%) as *n*-hexane insoluble fraction.
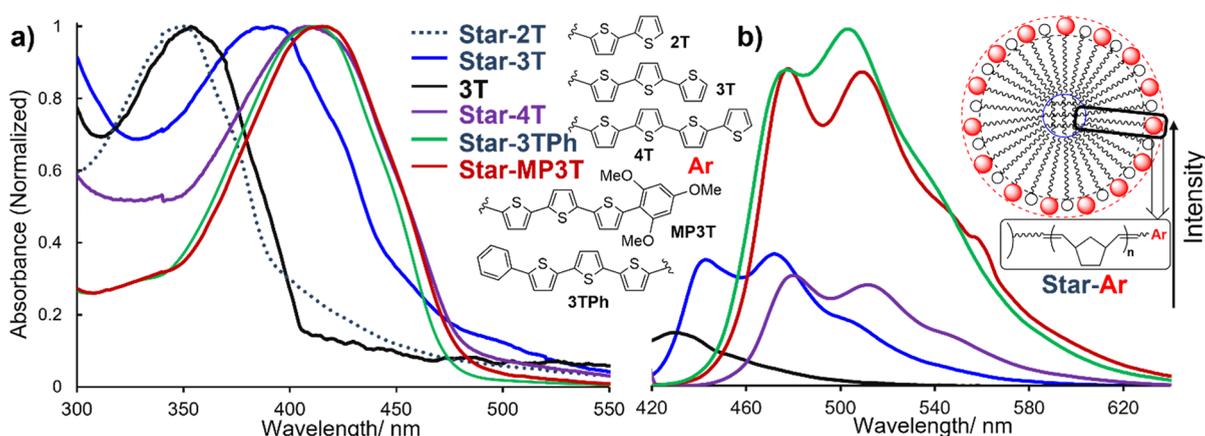
Figure 2. (a) UV−vis spectra [concentration 1.0×10^{-5} M in THF based on oligo(thiophene) units as estimated by the molar ratio at 25 °C] of different types of star-shaped polymers (**Star 2T**, **Star 3T**, **Star MP3T**, **Star 3TPh**, and **Star 4T**). (b) Fluorescence spectra of **Star 3T**, **Star MP3T**, **Star 3TPh**, and **Star 4T**. [Concentration 1.0×10^{-6} M in THF based on oligo(thiophene) units as estimated by the molar ratio at 25 °C, excitation at 390−415 nm (λ_{max} in the absorption)].

group, and terthiophene, should be close to facilitate the intramolecular interaction),[31] the observed difference could be explained as due to decrease in the intermolecular interaction in **Star-3TPh$_{50}$**. Taking into account these results, it is clear that both intermolecular and intramolecular interactions can be considered for the observed unique emission, and the fluorescence intensity through the intramolecular interaction should be affected by arm numbers (degree of cross-linking, core size) and the arm length between terthiophene and the phenyl group.

The concentration dependence of the emission spectra was also observed in **Star MP3T** (Figure 3 right) and **Star 3T** (Figure S7, Supporting Information); **A2-Star-MP3T** showed a higher fluorescence intensity than the others, whereas **CL$_{10}$-Star-3T** and then **Star-3T$_{50}$** exhibited better intensities. The above fact thus displays the precise placement of both the initiating fragments and the end-functional groups and demonstrates a prerequisite for exhibiting the unique emission, as well as proves the importance of our precise synthesis of star polymers.

2.3. Studies on the Optical Properties of Star/Linear 3TPh and Star/Linear 4T. *2.3.1. Steady-State Absorption and Fluorescence Spectra of Star/Linear 3TPh and Star/ Linear 4T.* Poly(NBE) is a transparent material (low optical absorbance) that possesses a rather linear structure with semirigidity of its backbone (containing a cyclic structure in the main chain);[43,46,47] the star-, ball-shaped structure with controlled diameters (close to the NBE repeat units) could be thus observed in the TEM micrographs.[29,32,43] In this section, we focus our discussion on comparison between "star" and "linear" polymers by using **Star-3TPh** ($M_n = 151\,000$, $M_w/M_n = 1.54$, run 2), **Linear 3TPh** ($M_n = 7000$, $M_w/M_n = 1.10$, Table S2, run S3), **Star 4T** ($M_n = 136\,000$, $M_w/M_n = 1.41$, run 14), and **Linear 4T** ($M_n = 7000$, $M_w/M_n = 1.03$, Table S2, run S5). As can be seen in Figure S10, their absorption bands could be ascribed to $\pi-\pi^*$ transitions within the conjugated end-functional groups (**3TPh/4T** and phenyl group), and no notable differences between the star-shaped and linear polymers were observed. On the other hand, fluorescence spectra vary among these polymers with respect to their vibronic band structures. To confirm whether the fluorescence is from an identical species or not in each polymer, we examined the fluorescence excitation spectra.
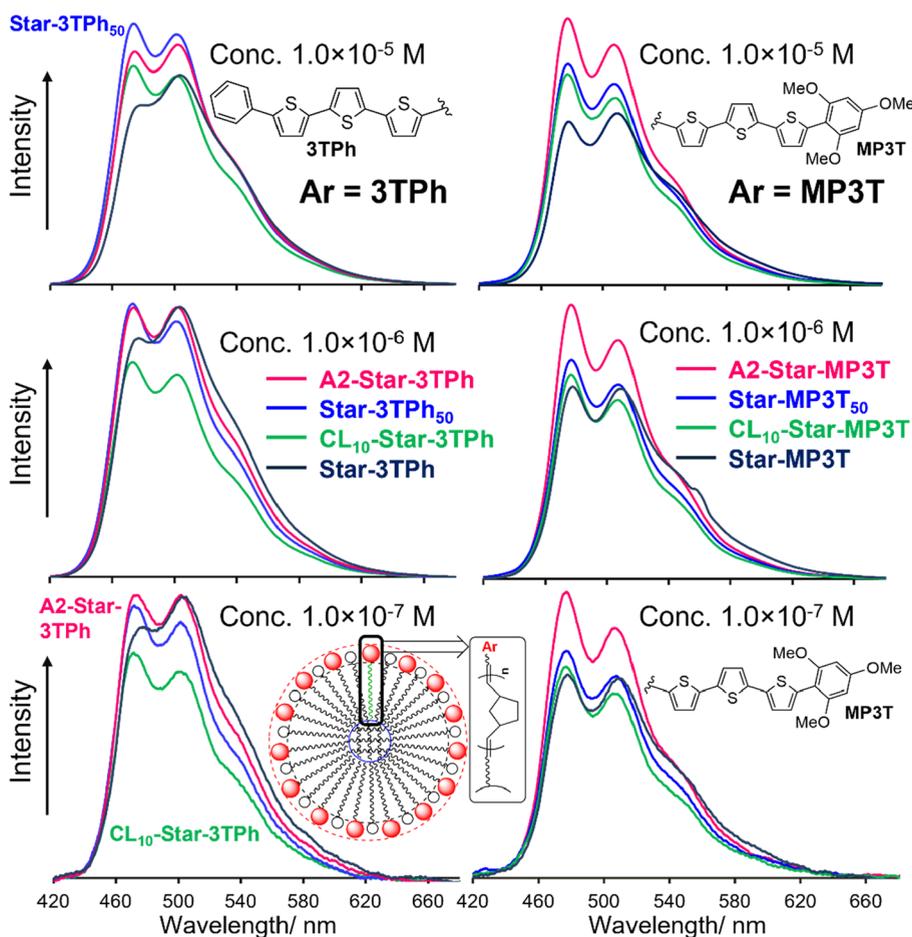
Figure 3. Fluorescence spectra of four types of (left) **3TPh**- and (right) **MP3T**-attached star-shaped polymers at different concentrations in THF at 25 °C with excitation at 410 nm. The additional spectra for **A2-Star-MP3T** and **A2-Star-3TPh** (with different concentrations) are shown in Figure S9, Supporting Information.

Figure 4 shows the fluorescence excitation spectra of **Star/Linear-3TPh** and **Star/Linear-4T**. As can be seen in the
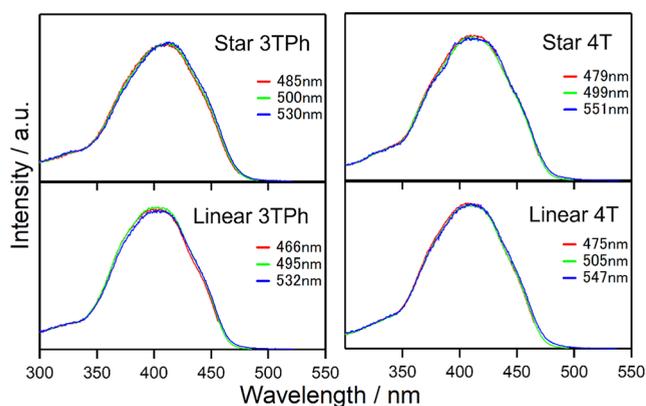
Figure 4. Monitored wavelength dependence of excitation spectra of **Star/Linear 3TPh** and **Star/Linear 4T** (normalized intensities).

figure, no monitored wavelength dependence was observed in all four polymers, indicating that only one species absorbs light preceding emission in each polymer sample. Moreover, the excitation spectra (Figure 4) are highly matched with the UV–vis absorption spectra, suggesting that there are no other species involved in polymers, that is, the present polymers are

of quite pure quality. Therefore, the fluorescence quantum yields for four polymers (**Star-3TPh**, **Star-4T**, **Linear-3TPh**, and **Linear-4T**) were further studied for a better understanding of the emission properties of the materials. The wavelengths at the intensity maxima of absorption and emission spectra, along with fluorescence quantum yield in THF, are summarized in Table 2. Fluorescence quantum yields

Table 2. Fluorescence Quantum Yields of Star and Linear Polymers (Star 3TPh, Star 4T, Linear 3TPh, and Linear 4T)

samples	absorption λ_{max}/nm	emission λ_{max}/nm		fluorescence quantum yields/ϕ^a
Star 3TPh	412	475	500	0.13
Linear 3TPh	407	466	495	0.23
Star 4T	409	479	507	0.20
Linear 4T	409	475	505	0.27

^{a}Fluorescence quantum yields with excitation at 426 nm at room temperature.

of **Star 3T-Ph**, **Linear 3T-Ph**, **Star 4T**, and **Linear 4T** are 0.13, 0.23, 0.20, and 0.27, respectively. A slight redshift of **Star 3T-Ph** and **Star 4T** relative to the corresponding linear polymers (**Linear 3T-Ph** and **Linear 4T**, respectively) in the maximum emission wavelengths is observed, as shown in Table 2, accompanied by a decrease in their quantum yields. In

comparison to the **Linear 3T-Ph** and **Linear 4T**, fluorescence quantum yields of their star polymers account for 57 and 74%, respectively.

2.3.2. Dependence of Quantum Yields on the Linear Polymer and Star Polymer. To clarify the reason for the reduction in quantum yields of star polymers compared with the corresponding linear polymers, time-resolved fluorescence spectra of **Star 3TPh** and **Linear 3TPh** with delay times of 50, 150, and 400 ps from the excitation pulse were investigated in Figure 5. The spectral profiles of both **Star 3TPh** and **Linear**
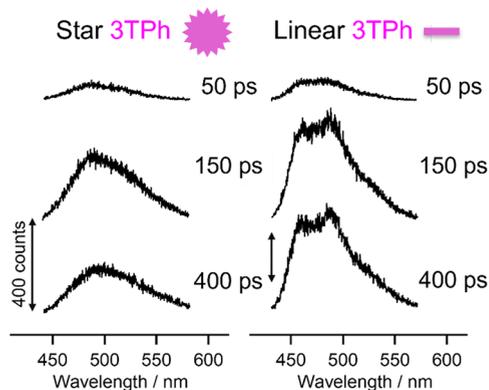
Figure 5. Time-resolved fluorescence spectra of star and linear polymers. Delay times from the laser excitation are indicated in the figure. The bar corresponds to 400 counts.

3TPh are less time-dependent, indicating no structural change in the excited state. The results of time-resolved fluorescence spectra of **Star 4T** and **Linear 4T** are consistent with those of **Star 3TPh** and **Linear 3TPh**.

Figure 6 shows time-resolved fluorescence signals of **Star/Linear 3TPh** and **Star/Linear 4T**. All of the decay profiles are
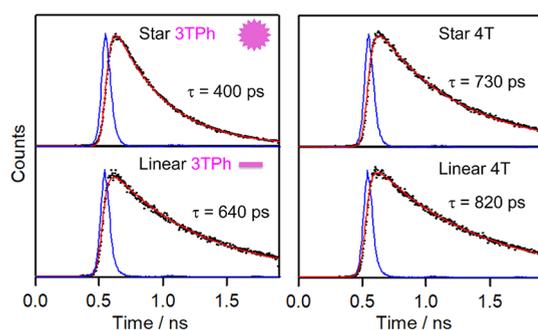
Figure 6. Time-resolved fluorescence signals of star and linear polymers excited at 406 nm in THF. Dots express counts of fluorescence signals, whereas the red lines are fittings and blue lines are instrumental responses. The vertical full scale is 6000 counts (**Star 3TPh**), 4600 (**Linear 3TPh**), 2800 (**Star 4T**), and 4300 counts (**Linear 4T**), respectively.

well fitted by a single-exponential decay function, and their fluorescence lifetimes τ are listed in Table 3. The fluorescence lifetimes of **Star 3TPh**, **Linear 3TPh**, **Star 4T**, and **Linear 4T** are 400, 640, 730, and 820 ps, respectively. Note that a longer fluorescence decay time constant for each linear polymer along with a higher quantum yield was observed than that of the corresponding star polymer.

It is noted that the observed quantum yields and fluorescence lifetimes in these star and linear polymers are

Table 3. Summary of Emission Lifetime (τ), Fluorescence Quantum Yield (ϕ), and the Calculated Radiative Rate Constant and Nonradiative Rate Constant (k_r and k_{nr}) of Star and Linear Polymers

samples	τ/ps	ϕ^a	k_r/s^{-1}	k_{nr}/s^{-1}
Star 3TPh	400	0.13	3.3×10^8	2.2×10^9
Linear 3TPh	640	0.23	3.6×10^8	1.2×10^9
Star 4T	730	0.20	2.7×10^8	1.1×10^9
Linear 4T	820	0.27	3.2×10^8	0.89×10^9

^{a}Fluorescence quantum yields with excitation at 426 nm at room temperature.

much larger than those of terthiophene ($\phi = 0.07$, $\tau = 160$ ps in benzene) and quaterthiophene ($\phi = 0.18$, $\tau = 440$ ps in benzene).[48] This is probably due to the effects of expanded π-conjugation over vinyl groups.

In general, quantum yields and lifetimes can be expressed as below[49]

$$\phi = k_r/(k_r + k_{nr}) \tag{1}$$

$$\tau = 1/(k_r + k_{nr}) \tag{2}$$

where k_r and k_{nr} are radiative and nonradiative rate constants, respectively. Based on the observed quantum yields and fluorescence lifetimes by using eqs 1 and 2, values of k_r and k_{nr} can be calculated, and the results are presented in Table 3.

It should be noted that the k_{nr} of **Star 3TPh** is enhanced by 1.8 times compared to that of **Linear 3TPh**, and the k_{nr} of **Star 4T** is 1.2 times higher than that of **Linear 4T**. The significant enhancement of k_{nr} in star-shaped polymers is attributable to an increase in vibrational modes due to the larger sizes of molecules. The larger number of molecular vibrational modes leads to nonradiative transitions by taking roles as promoting and accepting modes. In addition, the redshifts in star-shaped polymers from the corresponding linear polymers may cause an increase in nonradiative decay rates.

3. CONCLUDING REMARKS

The facile one-pot synthesis of highly branched soluble star-shaped polymers containing oligo(thiophene)s has been demonstrated by adopting the living ROMP technique using a molybdenum-alkylidene initiator by simple sequential additions of NBE and a cross-linker coupled with Wittig-type cleavage with an aldehyde in the termination step. The precise placement of both the initiating fragments and the end-functional oligo(thiophene)s is a prerequisite for exhibiting the present unique emission. The unique emission property of the star polymer can be well-maintained at a low concentration *via* controlling the size and arms.

Fluorescence lifetime and fluorescence quantum yield of star/linear polymers with **3TPh** and **4T** as end groups were measured in solution. Radiative and nonradiative constants were estimated. The increased fluorescence lifetime and fluorescence quantum yield of both linear and star polymers functionalized by **4T** was observed compared with those of **3TPh**, mainly caused by a decrease in nonradiative decay. Furthermore, linear polymers possess high values of fluorescence lifetime and quantum yield in comparison with their star polymers terminated with the same functional group because of a decrease in nonradiative decay; however, the values are still comparable to their linear polymers.

Unique emission properties through a space interaction on the star-shaped (non-conjugated) ROMP polymer surface, demonstrated in this work, should provide new possibilities for the design of new functional materials. The results should thus introduce a promising possibility of precision synthesis of star-shaped polymers, placing functionality on the surface.

4. EXPERIMENTAL SECTION

4.1. General Experimental Procedure. All experiments were conducted in a vacuum atmosphere dry box or by using vacuum/nitrogen lines called Schlenk techniques under a nitrogen (N_2) atmosphere. Chemicals of reagent grades were purified by the standard procedures. Toluene was stored over sodium/potassium alloy after pretreatment in a bottle containing molecular sieves (mixture of 3A 1/16, 4A 1/8, and 13X 1/16) from the commercially available one (anhydrous grade, Kanto Chemical Co., Inc.) in the dry box; the polymerization grade toluene was obtained after passing through an alumina flush short column of the supernatant clear solution under N_2. **Mo cat**[10,12,50] and CL 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo-endo*-dimethanonaphtalene (*exo/endo* = 0.15:1.00) were prepared according to the previous reports.[44] **2T-CHO** and **3T-CHO** were used in the dry box as received (Aldrich Chemical Co.) without further purification. **3TPh-CHO**, **MP3T-CHO**, and **4T-CHO** were prepared according to the previous report.[51]

All ^{1}H and ^{13}C NMR spectra (for confirmation of oligothiophenes[51] and polymers) were measured on a Bruker AV500 spectrometer (^{1}H, 500.13 MHz; ^{13}C, 125.77 MHz). All spectra were obtained in the deuterated solvent indicated at 25 °C, and the chemicals shifts (in ppm) are referenced to SiMe$_4$. Gel-permeation chromatography (GPC) (Shimadzu Co. Ltd.), equipped on a Shimadzu SCL-10A using a RID-10A detector (Shimadzu Co. Ltd.), was used for the measurement of molecular weights and the molecular weight distributions of the resultant *star*-shaped polymers. GPC measurements were conducted at 40 °C in THF (HPLC grade, Wako Pure Chemical Ind., Inc., degassed prior to use) with the addition of 2,6-di-*tert*-butyl-*p*-cresol (0.03 wt %) at a flow rate of 1.0 mL/min. The molecular weights were estimated on the basis of calibration curves using standard polystyrene samples through GPC columns (ShimPAC GPC-806, 804 and 802, 30 cm × 8.0 mm ϕ).

UV−vis spectra (concn 1.0×10^{-5} M in THF at 25 °C) for the resultant polymers were measured by Jasco V-650 UV−vis spectrophotometer, and the fluorescence spectra (ex. 1.0×10^{-6} M in THF at 25 °C) were measured by Hitachi F-7000 fluorescence spectrophotometer or a Horiba FluoroMax 4 spectrophotometer. The resultant polymers were excited at 350−415 nm. The polymer samples were excited at 406 nm by a light pulser Hamamatsu model PLP-10-040 (fwhm 70 ps) for the measurement of time-resolved fluorescence. Emission was dispersed by a Chromex 250IS imagine spectrograph and detected by a CCD streak scope Hamamatsu model C4334. Both time- and wavelength-resolved data were acquired on a personal computer and then analyzed using lab-made programs. Fluorescence quantum yields of samples were determined relative to that of the PFV oligomer, of which quantum yield was determined as 0.86 in toluene, as described previously.[52]

4.2. Synthesis of Star/Linear Polymers Containing Different End-Functional Groups, and Synthesis of 3TPh-CHO, MP3T-CHO, and 4T-CHO. Typical polymer-ization procedure (run 2, approach 1, Table 1) is as follows.[29−35] Into a toluene solution (10.0 g) containing NBE (25 equiv to Mo, 1.25 mmol, 118 mg), Mo(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(O^{t}Bu)$_2$ (2.00×10^{-5} mol) dissolved in toluene (1.0 g) was added in one portion at 25 °C (room temperature). After stirring the reaction mixture for 4 min, a toluene solution (4.0 g) containing 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo-endo*-dimethanonaphtalene (CL, 15 equiv to Mo, 0.75 mmol, 119 mg) was added. The solution was stirred for an additional 50 min. Moreover, into the reaction mixture, a toluene solution (5.0 g) containing NBE (25 equiv to Mo, 1.25 mmol, 118 mg) was added in one portion; the solution was further stirred for 15 min. The polymerization was terminated by the addition of **3TPh-CHO** (excess), and the solution was continuously stirred for an additional 1 h for completion. The mixture was then removed *in vacuo* until it was dissolved in the minimum amount of toluene. The solution was poured dropwise into cold *n*-hexane (precooled at −30 °C in the dry box) to afford light yellow precipitates. The polymer was then collected by filtration and dried *in vacuo*. The basic procedure in approach 2 was the same, except that a mixed solution containing CL and NBE (5.0 equiv to **Mo** in toluene) was added after the initial reaction of 25 equiv of NBE with **Mo** (second step). ^{1}H NMR (CDCl$_3$ at 25 °C) for the star-shaped poly(NBE) main chain: δ 5.34 and 5.21 (br m, 2H, olefinic), 2.79 and 2.42 (br s, 2H), 1.86 and 1.03 (m, 2H), 1.78,s and 1.35 (m, 4H) ppm. Resonances corresponding to different thiophene end groups 7.00−7.40 (thiophene) were also observed.

Typical linear polymer synthesis procedure: linear ring-opened poly(NBE) containing 3T-Ph as the chain end (**Linear 3TPh**) was prepared under the same conditions except that **3TPh-CHO** was added for termination after the reaction with NBE (only the 1st step in Scheme 2).

■ ASSOCIATED CONTENT

Ⓢ🛈 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c00739.

> Additional data for polymer synthesis, additional UV−vis and fluorescence spectra for polymer samples in THF, temperature-dependent UV−vis and fluorescence spectra in THF, and time-resolved emission spectra of **Star/Linear 4T** (PDF)

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Notes
The authors declare no competing financial interest.

■ ADDITIONAL NOTE

[a]According to the method employed previously,[29,35] the number of arms containing oligothiophene moieties in the resultant star-shaped ROMP polymers could be speculated on the basis of GPC data for poly(NBE)$_{25}$ (linear ROMP polymer prepared with 25 equiv of NBE, M_n = 2350 by GPC in THF *vs* polystyrene standards) and poly(NBE)$_{50}$ (M_n = 4710).[34] It was thus speculated that the resultant star-shaped ROMP polymers [runs 2 and 4, M_n = 15 100, 236 000 (for 3T-Ph); runs 10 and 12, M_n = 15 000, 279 000 (for MP3T), respectively] possessed *ca.* 36 (3T-Ph), 55 (MP3T) poly(NBE) arms containing the oligothiophene moiety. However, the exact arm numbers could not be estimated in the present study and the reported studies.[16−36]

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