

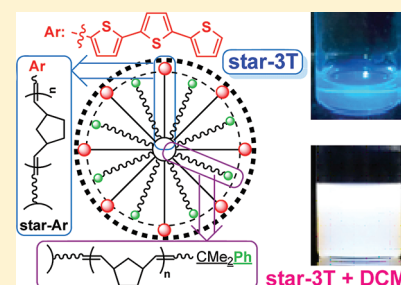
Synthesis of Oligo(thiophene)-Coated Star-Shaped ROMP Polymers: Unique Emission Properties by the Precise Integration of Functionality

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S Supporting Information

ABSTRACT: A facile synthesis of oligo(thiophene)-modified (coated) “soluble” star (ball)-shaped polymers has been achieved via sequential living ring-opening metathesis polymerization (ROMP) of norbornene and a cross-linking reagent using $\text{Mo}(\text{CHCMe}_2\text{Ph})(\text{N}-2,6\text{-iPr}_2\text{C}_6\text{H}_3)(\text{O}^t\text{Bu})_2$ as the initiator and oligo(thiophene) carbox-aldehydes for termination. The resultant star-shaped ROMP polymers containing ter- and tetrathiophene moieties exhibit unique emission properties due to an integration of the ROMP polymers (arranged functionalities): the blue emission was tuned to the white emission upon addition of 2-[2-[(*E*)-4-(dimethylamino)styryl]-6-methyl-4H-pyran-4-ylidene]malononitrile.



INTRODUCTION

Star-shaped polymers containing multiple linear arms connected at a central branched core represent one of the simplest nonlinear polymers,^{1,2} and synthetic studies using living polymerizations (with the absence of undesirable side reactions such as chain transfer and termination), especially atom transfer radical polymerization (ATRP),³ have thus been reported recently.^{2d,f,g,4} The synthesis of cross-linked polymers by ring-opening metathesis polymerization (ROMP)⁵ has also been known,^{6–9} and we recently demonstrated a controlled synthesis of “soluble” star polymers by the living ROMP technique using a molybdenum-alkylidene initiator by simple sequential additions of norbornene (NBE) and a cross-linker;⁸ the exclusive introduction of a functionality into the chain end can easily be achieved by adopting this approach.^{8,10,11} We also demonstrated that poly(9,9-di-*n*-octylfluorene-2,7-vinylene)s containing oligo(thiophene) moieties at the chain ends show unique emission properties resulting from intramolecular energy transfer.¹² Since unique emission properties would be expected to arise from placement of functionalities in a precise manner through weak interactions, we herein present a facile synthesis of oligo(thiophene)-modified star (ball)-shaped ROMP polymers that exhibit unique emission properties resulting from the precise assembled arrangement (Scheme 1).¹³

RESULTS AND DISCUSSION

According to our previous communication,^{8a} the method consists of the three key steps outlined in Scheme 1. $\text{Mo}(\text{CHCMe}_2\text{Ph})(\text{N}-2,6\text{-iPr}_2\text{C}_6\text{H}_3)(\text{O}^t\text{Bu})_2$ (**Mo**) was chosen as the initiator because of its ability to prepare the multiblock ring-opened copolymers in a precise manner with complete conversion of monomers,^{10,11} and 1,4,4a,5,8,8a-hexahydro-

1,4,5,8-*exo-endo*-dimethanonaphthalene (**CL**, *exo:endo* = 0.17:1.00)¹⁴ was chosen as a cross-linking reagent. The polymerization was terminated with various aldehydes [**ArCHO**, **Ar** = oligo(thiophene)s such as 2,2':5',2"-terthiophene (**3T**), 5-(2,4,6-trimethoxyphenyl)-2,2':5',2"-terthiophene (**MP3T**), and 3,3'''-dihexyl-2,2':5',2":5",2'''-quaterthiophene (**DH4T**); Scheme 1]. The results are summarized in Table 1.¹⁵

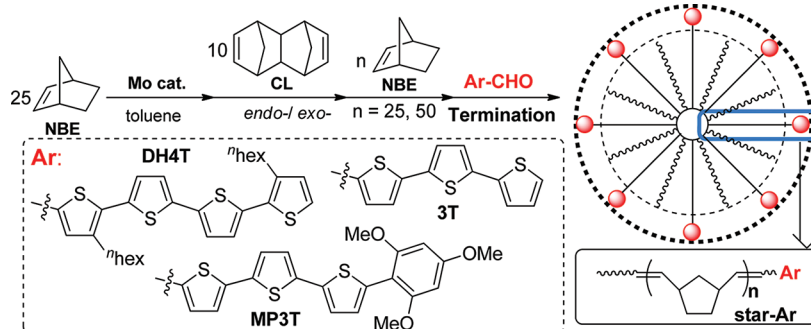
It turned out that the resultant polymers terminated with various aldehydes (**3T-CHO**, **MP3T-CHO**, **DH4T-CHO**) were high-molecular-weight ring-opened polymers with uniform molecular weight distributions [$M_n = (7.05\text{--}9.02) \times 10^4$, $M_w/M_n = 1.20\text{--}1.36$; runs 1, 2, 4, and 5),¹⁵ that were highly soluble in ordinary organic solvents such as toluene, tetrahydrofuran (THF), dichloromethane, and chloroform. The M_n values were similar to those for previously reported polymers terminated with 4-pyridinecarboxaldehyde (4- $\text{C}_5\text{H}_4\text{NCHO}$) and 4-trimethylsiloxybenzaldehyde (4- $\text{Me}_3\text{SiOC}_6\text{H}_4\text{CHO}$) obtained under the same conditions (runs 6 and 7).^{8a} These facts suggest that preparations of end-functionalized polymers (introduction of functionalities onto the surface of the star-shaped polymers) were achieved using this approach. The M_n values in the resultant ROMP polymers increased when the amount of NBE in the third polymerization was increased (25 $\rightarrow$ 50 equiv relative to **Mo**; runs 1–3).¹⁶ The increase in the M_n value was larger than that for linear poly(NBE), strongly suggesting the formation of star-shaped polymers.¹⁶

Figure 1 shows UV-vis and fluorescence spectra (in THF at 25 °C) for the resultant star-shaped polymers containing oligo(thiophene)s. The absorption bands in **star-3T** (388 nm)

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Scheme 1. Synthesis of Oligo(thiophene)-Modified Star-Shaped Polymers by Living ROMP of Norbornene

Table 1. Selected Results for Syntheses of Modified Star (Ball)-Shaped Polymers by Sequential Additions of NBE and CL in ROMP using Mo in Toluene^a

run	Ar-CHO ^b	n ^c	10 ⁻⁴ M _n ^d	M _w /M _n ^d	yield (%) ^e
1	3T-CHO	25	9.00	1.36	92.1
2	3T-CHO	25	9.02	1.20	92.1
3	3T-CHO	50	13.8	1.41	>99.9
4	MP3T-CHO	25	7.05	1.30	90.2
5	DH4T-CHO	25	7.80	1.23	81.3
6 ^f	4-C ₅ H ₄ NCHO	25	8.47	1.42	95
7 ^f	4-Me ₃ SiOC ₆ H ₄ CHO	25	8.97	1.31	95

^aConditions for the first reaction in Scheme 1: Mo cat. (1.82×10^{-5} mol), NBE (25 equiv relative to Mo), toluene (10.0 g), 25 °C, 5 min. Detailed procedures are described in the SI.¹⁵ ^bAldehyde for termination; structures of 3T, MP3T, and DH4T are shown in Scheme 1. ^cStarting feedstock ratio in the third step in Scheme 1. ^dObtained from GPC in THF vs polystyrene standards. ^eIsolated yields. ^fCited from ref 8a.

and star-DH4T (400 nm) were shifted to longer wavelength relative to those in 3T (354 nm) and DH4T (376 nm), respectively. The emission-peak maxima in star-DH4T (479 and 508 nm) were shifted to longer wavelength relative to those in star-3T (442 and 472 nm) and were relatively close in region to those in star-MP3T (486, 504, and 527 nm).

As shown in Figure 2, a notable increase in the emission intensity of star-3T relative to 3T was observed (5.0×10^{-7} M in THF at 25 °C), and the emission bands of star-3T observed at 442 and 472 nm in addition to shoulders at 497, 510, and 538 nm were apparently different from those in 3T and 5-vinyl-2,2':5',2''-terthiophene (3T-vinyl) (434 and 455 nm), corre-

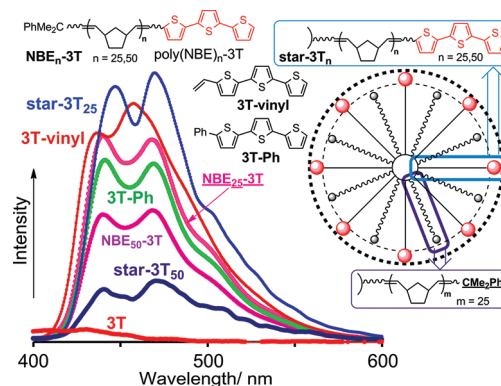


Figure 2. Fluorescence spectra of 3T, star-3T, 3T-Ph, 3T-vinyl, and 3T-attached poly(NBE) (NBE_n-3T) [$n = 25, 50$; concentration 5.0×10^{-7} M on the basis of oligo(thiophene) units as estimated by the molar ratio] in THF at 25 °C with excitation at 380 nm.¹⁷

sponding to the end fragment by termination with aldehyde. Marked differences in the emission spectra of star-3T were not observed upon variation of the solvent or temperature.¹⁷ In contrast, it should be noted that a significant decrease in the emission intensity in star-3T was observed when the number of NBE repeat units in the third polymerization step was increased from 25 to 50 (star-3T₂₅ vs star-3T₅₀ in Figure 2).

It is noteworthy that the absorption band observed in the UV-vis spectrum and the emission pattern observed in the fluorescence spectrum of star-3T were close to those of the phenyl-substituted terthiophene 5-phenyl-2,2':5',2''-terthiophene (3T-Ph).¹⁷ Moreover, as exemplified in Figures 2 and

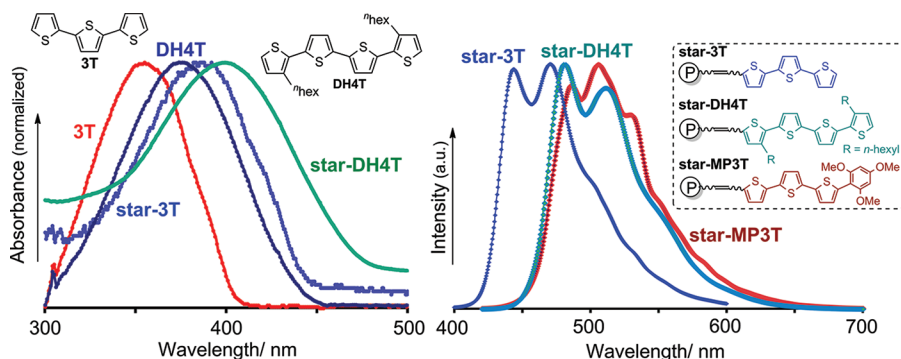


Figure 1. (left) UV-vis spectra of 3T, star-3T, DH4T, and star-DH4T and (right) fluorescence spectra of star-3T, star-MP3T, and star-DH4T (excitation at 380 nm). The concentration was 1.0×10^{-6} M [on the basis of oligo(thiophene) units as estimated by the molar ratio] in THF at 25 °C.

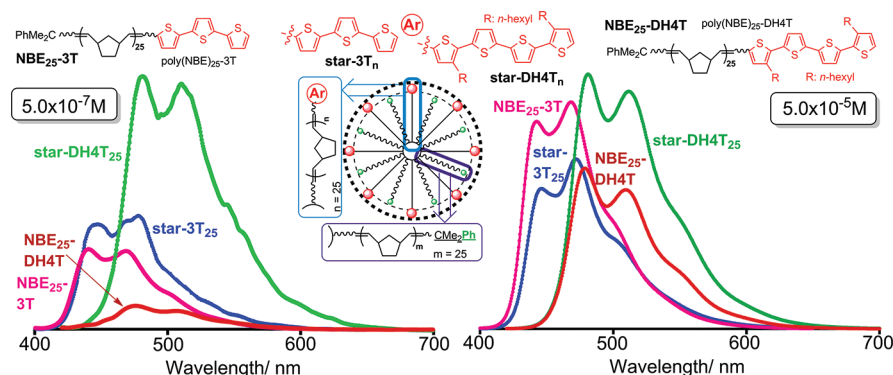


Figure 3. Fluorescence spectra of star-3T_{25} , 3T-attached poly(NBE) ($\text{NBE}_{25}\text{-3T}$), star-DH4T_{25} , and DH4T-attached poly(NBE) ($\text{NBE}_{25}\text{-DH4T}$) at different concentrations in THF at 25 °C with excitation at 380 nm.¹⁷

3, the emission bands in star-3T and star-DH4T were close to those of the corresponding linear ring-opened polymers $\text{NBE}_n\text{-3T}$ ($n = 25, 50$) and $\text{NBE}_{25}\text{-DH4T}$. The emission intensities in these linear polymers were dependent upon the number of NBE repeating units ($\text{NBE}_{25}\text{-3T}$ vs $\text{NBE}_{50}\text{-3T}$).¹⁹ Moreover, the emission intensities of $\text{NBE}_{25}\text{-3T}$ and $\text{NBE}_{25}\text{-DH4T}$ were strongly affected by the concentration, and trends in the relative intensities opposite to those for star-3T were observed as the concentration was varied (Figure 3): the intensities of the linear polymers remarkably increased at higher concentration (Figure 3 right) and decreased drastically at low concentration (Figure 3 left). This fact would suggest that an increase in the emission intensity (and shifts in both the emission maxima and the absorption bands) in star-3T would be due to a (weak) interaction of the 3T fragment with the phenyl group (existing in the ROMP polymer as the initiating fragment) in solution. A similar observation was also realized for star-DH4T , although an interaction with the phenyl group may not be as strong as for the terthiophene analogues (star-3T and NBE-3T), probably because of the *n*-hexyl substituent. Taking into account these facts, it is thus suggested that a precise placement (arrangement) of both the initiating fragment and the end-functional group are prerequisites for exhibiting the present unique emission (by a through-space energy transfer).

It is interesting to note that the blue-light emission of the THF solution containing star-3T (1.0×10^{-5} M) was simply tuned to white-light emission upon addition of a THF solution (3.2×10^{-6} M) containing the orange-red-emitting dye 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (DCM) (Figure 4).¹⁸ The white emission was not observed from THF solutions containing 3T and 3T-Ph and was difficult to tune by using linear polymers containing 3T at the chain end ($\text{NBE}_n\text{-3T}$). White-light-emitting diodes (WLEDs) have received considerable interest because of their

potential applications in full-color flat panel displays, etc.,¹⁹ and in particular, white polymer light-emitting diodes (WPLEDs) are promising because of their great potential of flexibility and easy solution processing.²⁰ Although studies of the efficiency of the resultant polymers and the detailed mechanism are still in progress, this might be a unique candidate for the preparation of white-light-emitting materials based on star-shaped polymers.²¹

CONCLUSION

We have demonstrated that a facile synthesis of “soluble” star-shaped polymers containing oligo(thiophene)s has been accomplished in a precise manner by adopting the living ROMP technique using a molybdenum–alkylidene initiator by simple sequential additions of norbornene and the cross-linker. The resultant polymers, especially star-3T , exhibited unique emission properties that were observed by integration of the ROMP polymer (especially by placement of the initiating and end functionalities) in a precise manner. As far as we know, this is the first example of not only the precise synthesis of star-shaped polymers modified with conjugated molecules but also the demonstration of unique emission properties through integration of functionalities. We thus believe that the method would provide new possibilities for applications of the star-shaped polymers as new performance materials.

ASSOCIATED CONTENT

Supporting Information

Experimental details and additional UV–vis and fluorescence spectra for the resultant star polymers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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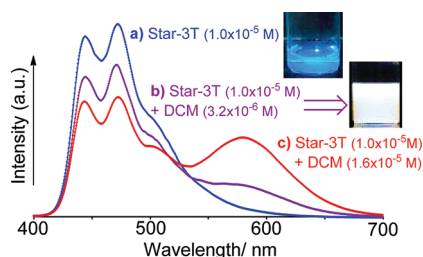


Figure 4. Fluorescence spectra of star-3T upon addition of DCM in THF at 25 °C with excitation at 380 nm.

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- (17) Additional UV–vis and fluorescence spectra are shown in the SI.
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