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

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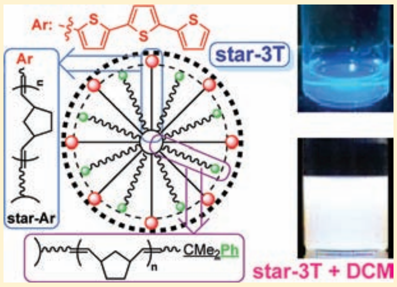
Supporting Information

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 Mo(CHCMe$_2$Ph)(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(O^{t}Bu)$_2$ as the initiator and oligo(thiophene) carboxaldehydes 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-4*H*-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. Mo(CHCMe$_2$Ph)(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(O^{t}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 = (7.05−9.02) × 10^4, M_w/M_n = 1.20−1.36; 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-C_5H_4NCHO) and 4-trimethylsiloxybenzaldehyde (4-$Me_3SiOC_6H_4CHO$) 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 → 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

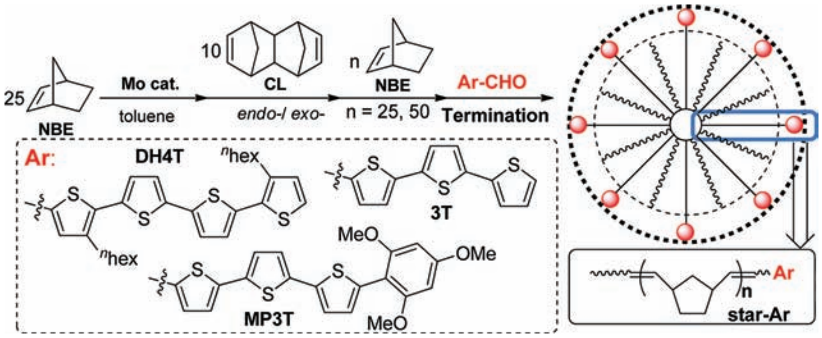

Table 1. Selected Results for Syntheses of Modified Star (Ball)-Shaped Polymers by Sequential Additions of NBE and CL in ROMP using Mo in Toluene[a]

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_5H_4NCHO	25	8.47	1.42	95
7[f]	4-$Me_3SiOC_6H_4CHO$	25	8.97	1.31	95

[a] Conditions 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] [b] Aldehyde for termination; structures of **3T**, **MP3T**, and **DH4T** are shown in Scheme 1. [c] Starting feedstock ratio in the third step in Scheme 1. [d] Obtained from GPC in THF vs polystyrene standards. [e] Isolated yields. [f] Cited from ref 8a.

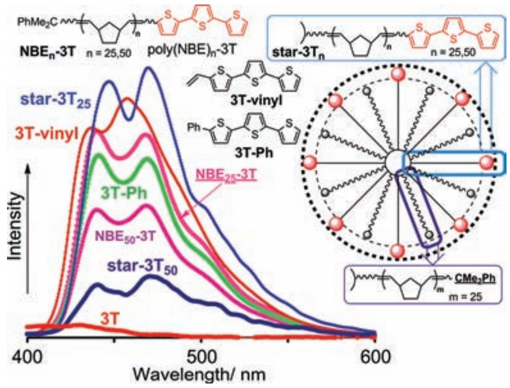

Figure 2. Fluorescence spectra of **3T**, **star-3T**$_n$, **3T-Ph**, **3T-vinyl**, and **3T**-attached poly(NBE) (**NBE**$_n$**-3T**) [n = 25, 50; concentration 5.0×10^{-7} M on the basis of oligo(thiophene) units as estimated by the molar ratio] in THF at 25 °C with excitation at 380 nm.[17]

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), corresponding 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-3T**$_{25}$ vs **star-3T**$_{50}$ 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

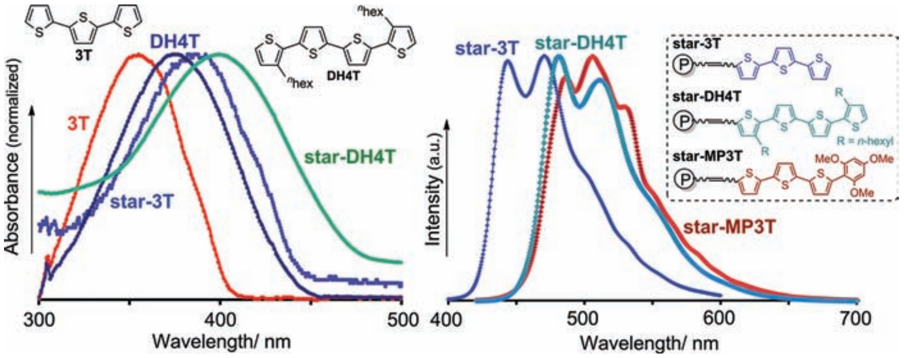

Figure 1. (left) UV–vis spectra of **3T**, **star-3T**, **DH4T**, and **star-DH4T** and (right) fluorescence spectra of **star-3T**, **star-MP3T**, and **star-DH4T** (excitation at 380 nm). The concentration was 1.0×10^{-6} M [on the basis of oligo(thiophene) units as estimated by the molar ratio] in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

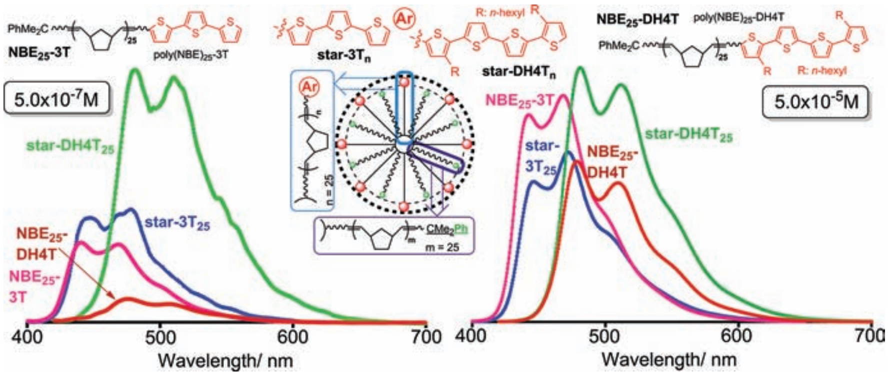

Figure 3. Fluorescence spectra of **star-3T$_{25}$**, **3T**-attached poly(NBE) (**NBE$_{25}$-3T**), **star-DH4T$_{25}$**, and **DH4T**-attached poly(NBE) (**NBE$_{25}$-DH4T**) at different concentrations in THF at 25 °C with excitation at 380 nm.[17]

3, the emission bands in **star-3T** and **star-DH4T** were close to those of the corresponding linear ring-opened polymers **NBE$_n$-3T** (n = 25, 50) and **NBE$_{25}$-DH4T**. The emission intensities in these linear polymers were dependent upon the number of NBE repeating units (**NBE$_{25}$-3T** vs **NBE$_{50}$-3T**).[19] Moreover, the emission intensities of **NBE$_{25}$-3T** and **NBE$_{25}$-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)-4*H*-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 (**NBE$_n$-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]

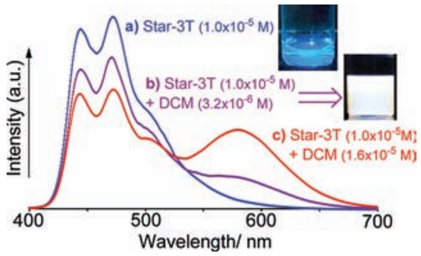

Figure 4. Fluorescence spectra of **star-3T** upon addition of DCM in THF at 25 °C with excitation at 380 nm.

■ 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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(16) Since the observed increase in the M_n value [ca. 48000 by gel-permeation chromatography (GPC) vs polystyrene standards from runs 1−3] was much higher than for the linear poly(NBE) analogues [increased by 25 NBE repeating units, 2354 by molecular weight, ca. 6400 for poly(NBE) terminated with **3T** by GPC vs polystyrene standards, as shown in the SI[15]] and also since the first polymerization of NBE proceeded with high conversion even after 5 min,[8a] the results suggest that the resultant ROMP polymers are star-shaped polymers consisting of a core and NBE branches (first and third polymerization). As described previously,[8a] the number of polymer chains (arms after the third polymerization) may be simply assumed on the basis of the observed increase in the M_n values and the M_n value of the linear poly(NBE) (increased by 25 NBE repeat units). The value (48000/6400 = 7.5, the total number of arms from first and third polymerization was assumed as 14 or 16) is close to or relatively smaller than that reported previously,[8a] suggesting that the resultant polymers are star-shaped polymers consisting of a core and NBE branches.

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

(18) The blue emission of the nanoparticles containing oligofluorene was tuned to the white emission upon addition of DCM. See: Vijayakumar, C.; Sugiyasu, K.; Takeuchi, M. *Chem. Sci.* **2011**, *2*, 291.

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