npg

ORIGINAL ARTICLE

Synthesis and optical properties of poly(*N*-octyl-*m*-benzamide)s bearing an oligothiophene chromophore on the benzene ring

Koji Takagi, Yuma Nishikawa, Kana Shimizu, Ryohei Yamakado, Shinri Sugimoto and Masaharu Kondo

The precise arrangement of π-conjugated molecules is of significant importance for applications in optoelectronic devices. We have previously demonstrated the potential utility of poly(*N*-alkyl-*p*-benzamide)s as a scaffold for this purpose. In this paper, we report a controlled chain-growth polymerization of methyl 3-octylaminobenzoate having a bithiophene chromophore at the 5-position of the benzene ring with improved polymerization activity, which gives poly(*N*-octyl-*m*-benzamide)s with better solubility. The introduction of a terthiophene chromophore at the propagating end is also described. From the spectroscopic data and theoretical investigations, it was found that neighboring bithiophene chromophores have π–π interactions, and the excited energy can migrate along the polymer chain.

INTRODUCTION

π-Conjugated molecules have attracted a significant attention in recent decades because of their unique optoelectronic characteristics. Because of the advancement of synthetic organic chemistry, particularly the discovery of metal-catalyzed carbon–carbon bond formation reactions, diversified π-conjugated molecules bearing tunable frontier molecular orbital energy and band gap energy can be obtained. The materials' performance in optoelectronic devices strongly depends on the arrangement of the constituent π-conjugated systems. Because the spatial arrangement of π-conjugated molecules, such as J- and H-aggregation, affects the through-space chromophore interaction,[1] the precise arrangement of π-conjugated molecules is important for obtaining desirable photophysical, electronic and electrochemical functional materials. In the case of a naturally-occurring DNA, for example, the double-stranded helical main chain forces basepairs to be stacked in the face-to-face arrangement, leading to the long distance charge transport along the main chain.[2–4] Many polymerization chemists have addressed this issue by utilizing a xanthene skeleton,[5–8] calix[4]arene scaffold,[9,10] 2-substituted trimethylene tether,[11–13] hydrogen-bonding ureidophthalimide unit[14–16] and π-conjugated dithienopyrrole backbone.[17,18] These polymers were synthesized by step-growth polymerization, and the charge/energy transfer and excimer emission were observed to demonstrate their potential application as optoelectronic materials. Nakano et al.[19–22] investigated the chain-growth polymerization of dibenzofulvene to figure out the unexpectedly high polymerization activity by anionic, free-radical and cationic initiators. On the basis of spectroscopic data,

single-crystal X-ray analyses and theoretical calculations, it was found that the polymer main chain adopts a nearly all-trans, slightly twisted conformation, and the fluorenyl groups on the side chains stack on top of each other. The specific conformation of poly(dibenzofulvene) eventually gave rise to the superior hole mobility comparable to that of the main chain π-conjugated poly(*p*-phenylenevinylene).[23,24] We previously prepared a series of poly(*N*-alkyl-*p*-benzamide)s having an oligothiophene chromophore on the benzene ring or at the end of an alkyl chain.[25,26] Ultraviolet-visible (UV-vis) absorption and fluorescence emission spectra suggested π–π interactions between oligothiophene chromophores in solution. However, the low polymerizability of monomers[25] and poor solubility of polymers[26] inhibited in-depth investigations. In this article, we describe the controlled polymerization of methyl 3-octylaminobenzoate having a bithiophene chromophore at the 5-position of the benzene ring. Because the large π-conjugated unit is separated from the polymerizing amino group, improved polymerization activity is expected (Figure 1). In addition, the obtained poly(*m*-benzamide)s should have better solubility compared with poly(*p*-benzamide)s. Yokozawa et al revealed the chiral conformation of poly(*m*-benzamide)s in solution.[27] Polymers consisting of *meta*-connected aromatic rings often adopt well-defined conformations.[28–30] Taking these facts into consideration, poly(*m*-benzamide)s are promising scaffolds to achieve the controlled arrangement of chromophores. The incorporation of a terthiophene chromophore at the propagating end was subsequently performed to clarify the excited-energy transfer mediated by the π–π interaction between chromophores.

Department of Materials Science and Engineering, Graduate School of Engineering, Nagoya Institute of Technology, Nagoya, Japan
Correspondence: Professor K Takagi, Department of Materials Science and Engineering, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso, Showa, Nagoya 466-8555, Japan.
E-mail: takagi.koji@nitech.ac.jp
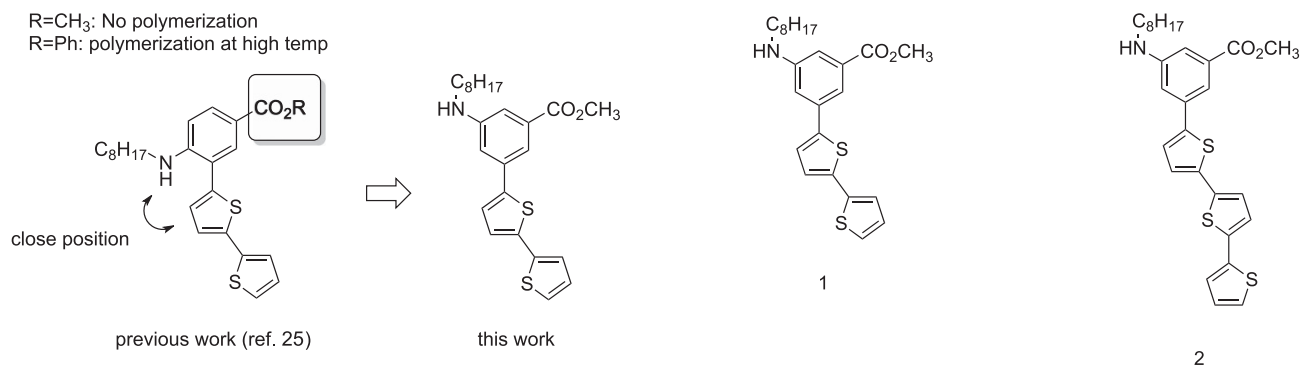
Figure 1 Monomer design for the improved polymerization activity.

Figure 2 Structures of **1**, **2** and model compounds (**M1** and **M2**).

EXPERIMENTAL PROCEDURE

Materials and instrumentations are described in the Supplementary information. Model compounds (**M1** and **M2**) were synthesized as reported previously.[31]

Methyl 3-(2′-(5′,2″-bithienyl))-5-octylaminobenzoate (1)

Pd(PPh₃)₄ (102 mg, 87.9 µmol) was added to a solution of methyl 3-bromo-5-octylaminobenzoate (1.7 g, 5.1 mmol)[31] and 5-tributylstannyl-2,2′-bithiophene (5.1 g, 11.1 mmol) in toluene (13 ml), and the mixture was heated to reflux overnight. After water was added, the aqueous phase was extracted with CH₂Cl₂. The combined organic phase was dried over MgSO₄, and solvents were removed by a rotary evaporator. Purification by SiO₂ chromatography (CH₂Cl₂: hexane = 1:1, R_f = 0.28) followed by recrystallization from CH₂Cl₂/hexane gave **1** at 1.1 g (53% yield). Yellow needle; Mp. 63–64 °C; ¹H-nuclear magnetic resonance (NMR) (600 MHz, CDCl₃) δ ppm 0.89 (t, J = 6.66 Hz, 3H), 1.24–1.37 (8H), 1.42 (m, 2H), 1.64 (m, 2H), 3.17 (t, J = 7.04 Hz, 2H), 3.82 (brs, 1H), 3.92 (s, 3H), 6.95 (s, 1H), 7.03 (t, J = 3.58 Hz, 1H), 7.14 (d, J = 3.58 Hz, 1H), 7.18 (s, 1H), 7.20 (d, J = 3.33 Hz, 1H), 7.22 (d, J = 5.12 Hz, 1H), 7.24 (d, J = 3.58 Hz, 1H), 7.59 (s, 1H); Anal Calcd for C₂₄H₂₉NO₂S₂: C, 67.41; H, 6.84; N, 3.28; S, 15.00%. Found: C, 67.20; H, 6.78; N, 3.18; S, 15.09%.

Methyl 3-nonylamino-5-(2′-(5′,2″,5″,2‴-terthienyl))benzoate (2)

This monomer was prepared following the synthetic method of **1**. Yellow needle; Mp. 88–89 °C; ¹H-NMR (200 MHz, CDCl₃) δ ppm 0.89 (t, J = 6.7 Hz, 3H), 1.48–1.18 (12H), 1.64 (m, 2H), 3.18 (t, J = 7.0 Hz, 2H), 3.89–3.70 (brs, 1H), 3.92 (s, 3H), 6.95 (t, J = 1.9 Hz, 1H), 7.02 (dd, J = 3.6, 5.0 Hz, 1H), 7.24–7.08 (7H), 7.59 (s, 1H); Anal Calcd for C₂₈H₃₁NO₂S₃: C, 65.97; H, 6.13; N, 2.75%. Found: C, 65.94; H, 6.20; N, 2.65%.

P1-OMe (polymerization of 1)

A solution of **1** (0.20 g, 0.47 mmol) in THF (0.5 ml) at 0 °C was added to a solution of lithium bis(trimethylsilyl)amide (LiHMDS) (1 M THF solution, 0.6 ml, 0.6 mmol) and phenyl 4-methylbenzoate (9.9 mg, 47 µmol) in THF (0.5 ml), and the mixture was stirred at room temperature overnight. After saturated aqueous NH₄Cl solution was added, the aqueous phase was extracted with CHCl₃. The combined organic phase was washed with brine, dried over MgSO₄ and poured into hexane to obtain **P1-OMe**. Mn = 3800 (Mw/Mn = 1.20); ¹H-NMR (600 MHz, CD₂Cl₂) δ ppm 0.71–0.96 (26H), 1.05–1.34 (72H), 1.63 (11H), 2.13 (3H), 3.57 (20H), 3.88 (3H), 6.70–7.55 (78H).

P1-2-OMe (attachment of terthiophene at the propagating end of P1-OMe)

KOH (35 mg) dissolved in water (0.3 ml) was added to a solution of **P1-OMe** (21 mg) in THF (0.2 ml), and the mixture was stirred at 40 °C for 6 h. After 1 M HCl was added, the aqueous phase was extracted with CH₂Cl₂. The combined organic phase was dried over MgSO₄ and poured into hexane to obtain **P1-OH**. Then, **2** (17 mg, 33 µmol), pyridine (0.2 ml) and SiCl₄ (5.3 µl, 47 µmol) were added to obtain **P1-OH** (10 mg), and the mixture was heated at 110 °C
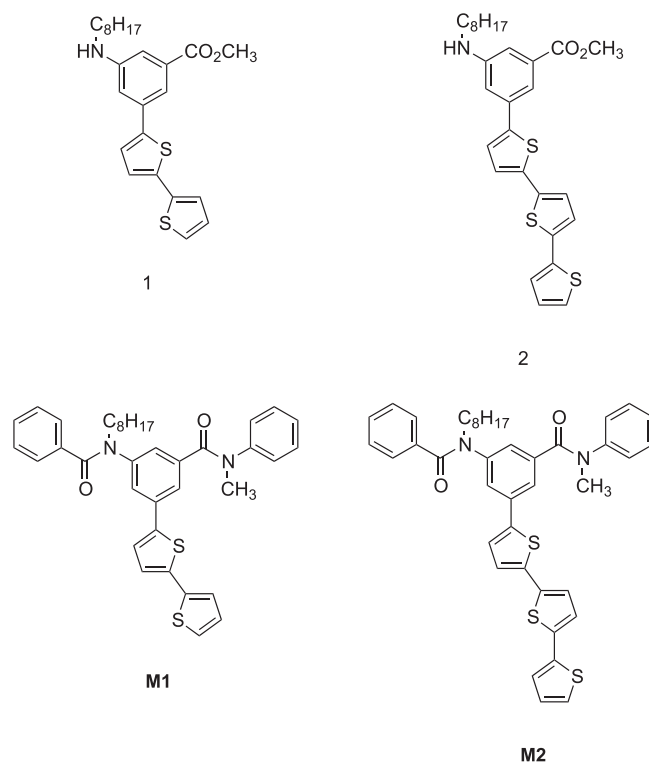
overnight. After the solvents were evaporated, ethyl acetate and water were added, and the aqueous phase was extracted with ethyl acetate. The combined organic phase was dried over MgSO₄ and concentrated to dryness. The crude product was dissolved in CHCl₃ and was poured into hexane to obtain 5 mg (38% yield) **P1-2-OMe**. Mn = 4600 (Mw/Mn = 1.12); ¹H-NMR (600 MHz, CD₂Cl₂) δ ppm 0.71–0.91 (39H), 1.01–1.36 (86H), 1.55 (27H), 2.13 (3 H), 3.57 (13H), 3.89 (3 H) and 6.78–7.44 (108 H).

RESULTS AND DISCUSSION
Synthesis

Methyl 3-octylaminobenzoates **1** and **2** with a bithiophene and terthiophene chromophore at the 5-position of the benzene ring, respectively, were prepared; and their purities were confirmed by NMR spectra and elemental analyses. The structures of **1** and **2,** along with those of the model compounds (**M1** and **M2**), are shown in Figure 2. According to Yokozawa's method,[32] the polymerization of **1** was conducted using LiHMDS (1.3 equiv) as a bulky base and phenyl 4-methylbenzoate as an initiator (Scheme 1).

The molecular weight distribution of **P1-OMe** was slightly broad when the polymerization was conducted at room temperature (Table 1, Entry 1). The addition of an initiator was essential to promote the smooth polymerization because a substantial amount of **1** was recovered in the polymerization without phenyl 4-methylbenzoate (Entry 2 and Figure 3). The polymerization at 0 °C gave **P1-OMe** with the number-averaged molecular weight of 3800 and a relatively narrow molecular weight distribution (1.20) (Entry 3). The number-averaged molecular weight increased to 6100 while maintaining the narrow molecular weight distribution (1.12) after decreasing the amount of initiator to 0.05 equiv (Entry 4). These results are in contrast to the polymerization of 4-octylaminobenzoates bearing a bithiophene chromophore at the 3-position of the benzene ring. In our earlier report, only phenyl 3-(2′-(5′,2″-bithienyl))-4-octylaminobenzoate with a good leaving group could be polymerized at elevated temperature in
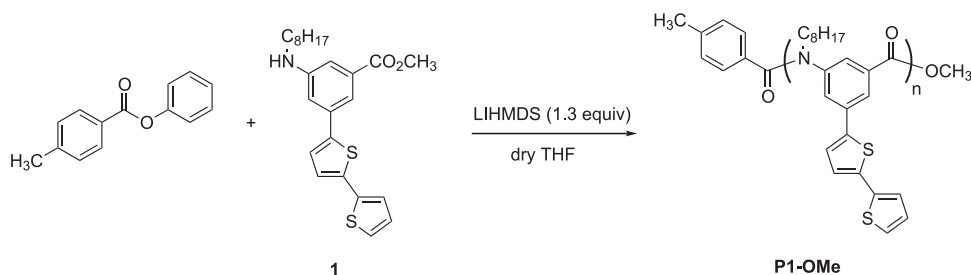
Scheme 1 Polymerization of **1**.

Table 1 Polymerization results of 1

Entry	Initiator/ equiv	Temperature/°C	Conversion/%[a]	Mₙ/PDI (GPC)[b]	Mₙ (NMR)[b]
1	0.1	Room temp	quant	6500/1.31	NA
2	0	0	NA	4700/1.32	NA
3	0.1	0	86	3800/1.20	3300
4	0.05	0	83	6100/1.12	5100

[a]Calculated from the ^{1}H-NMR spectra of crude polymerization mixture.
[b]Estimated by GPC based on standard polystyrene samples.

the presence of N,N,N',N'-tetramethylethylenediamine as an activator.[25] As we described in the introduction, the reactivity of the aminyl anion generated from **1** might be high because of the lower steric hindrance, although the electronic factor cannot be ruled out. In the ^{1}H-NMR spectrum of **P1-OMe**, the methyl proton signals at the initiating and propagating ends were unambiguously observed at 2.13 and 3.88 ppm, respectively, nearly in the same integral ratio (Supplementary Figure S3). By comparing the integral ratio of these proton signals with that of the methylene proton signals on the amide nitrogen in the repeat unit at approximately 3.6 ppm, the molecular weight of **P1-OMe** was calculated as 3300, which roughly agreed with the value estimated from the gel permeation chromatography (GPC) analysis.

The matrix-assisted laser desorption/ionization time-of-flight (MALDI-ToF) mass spectrum of **P1-OMe** was collected using dithranol as a matrix. The mass spectrum consisted of only one series of peaks, indicating that each polymer molecule has a unique end group (Figure 4). Observed peaks were expressed as $m/z = 395.2n + 119.1$ (*p*-toluoyl) + 31.0 (methoxy) + 23.0 (Na), where n is equal to the number of repeat units. Therefore, one end group of the polymer is a *p*-toluoyl group, and the other is a methoxy group. For example, the 11-mer of this distribution is expected to produce a signal at $m/z = 4524.6$, and the signal is actually observed at $m/z = 4524.1$. These facts suggest that the chain-growth polymerization of **1** proceeds in a controlled manner under the optimized condition.

Subsequently, a terthiophene chromophore was introduced at the propagating end of **P1-OMe**. In the first step, a THF solution of **P1-OMe** was treated with an aqueous KOH solution at 40 °C for 6 h to obtain **P1-OH** bearing the carboxylic acid terminal group. The number-averaged molecular weight was almost same as that of **P1-OMe**, and the narrow molecular weight distribution (1.16) was maintained. In the ^{1}H-NMR spectrum of **P1-OH**, a proton signal assignable to the methyl ester at 3.88 ppm disappeared. In the second step, **P1-OH** was subjected to condensation with **2** using SiCl$_4$ in pyridine at 110 °C overnight. The number-averaged molecular weight of **P1-2-OMe** increased to 4600. The MALDI-ToF mass spectrum still
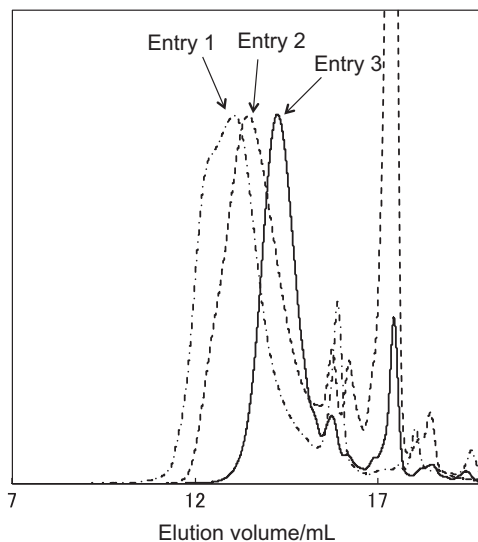
Figure 3 GPC profiles of the crude product of **P1-OMe** (the peak eluted at approximately 17 ml is recovered **1**).

consisted of only one series of peaks. Compared with the spectrum of **P1-OMe**, each peak was shifted to the larger molecular weight region by $m/z = 478.3$, which corresponds to the molecular weight of the attached terthiophene chromophore (477.1) (Supplementary Figure S5). For example, the 11-mer of this distribution is expected to produce a signal at $m/z = 5002.3$, and the signal is actually observed at $m/z = 5003.2$. On the basis of these data, **P1-2-OMe** also has a well-defined primary structure, namely, a number of bithiophene chromophores in the repeat unit and one terthiophene chromophore at the propagating end.

Optical properties

The UV-vis absorption and fluorescence emission spectra of **P1-OMe** and **P1-2-OMe,** together with the low molecular weight model compound **M1,** were collected in CHCl$_3$ solution. As shown in Figure 5, the peak maxima of absorption (348 nm) and emission (430 nm) of **P1-OMe** exhibited small hypsochromic and apparent bathochromic shifts, respectively, compared with **M1** (351 and 422 nm) with one bithiophene unit. These peak shifts are coincident with our previous reports,[25,26] and the bithiophene chromophores in the repeat unit are supposed to have π–π interactions. The relative fluorescence quantum yields of **M1** and **P1-OMe** were 0.04 and 0.03, respectively. The UV-vis absorption spectrum of **P1-2-OMe** showed a shoulder peak at approximately 430 nm, originating from a terthiophene chromophore, in addition to the peak maximum at 348 nm. Because a terthiophene chromophore only exists at the propagating
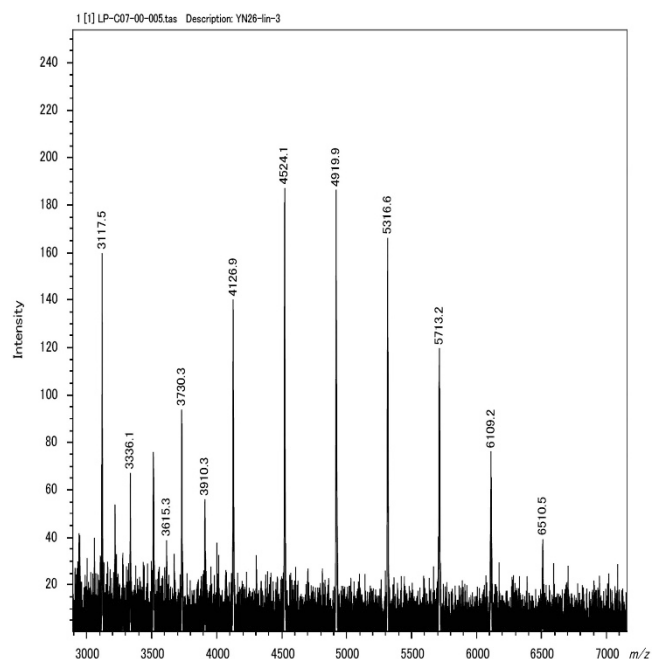
Figure 4 MALDI-ToF mass spectrum of **P1-OMe**.

Figure 5 (**a**) UV-vis and (**b**) fluorescence spectra of **M1**, **P1-OMe** and **P1-2-OMe** in CHCl$_3$ solution (10^{-5} M). The excitation wavelengths of the materials were the absorption maxima.

end, the small absorbance of this peak is reasonable. In contrast, the intensity of the emission peak centered at 430 nm was decreased considerably, and a new emission band was observed at 456 nm for **P1-2-OMe**. The relative fluorescence quantum yield of **P1-2-OMe** was 0.07. To elucidate the origin of this longer wavelength emission, the spectra of a CHCl$_3$ solution of a mixture containing **P1-OMe** and **M2** with one terthiophene unit, abbreviated here as the mixed system, were also measured for comparison (Supplementary Figure S6). The molar ratio of bithiophene:terthiophene was 10:1 to be consistent with that of **P1-2-OMe**. Although the absorption spectra were analogous, the emission spectra were different between **P1-2-OMe** and the mixed system. The emission peak maximum of the mixed system was observed at 432 nm, and the spectral pattern was almost identical to that of **P1-OMe** with no terthiophene chromophore. The emission spectrum of **P1-OMe** and the absorption spectrum of **M2** overlap (Supplementary Figure S7). Because unambiguous shifts of the NMR proton signals were not observed when going from **M1** to **P1-OMe**, the density functional theory calculation was performed to obtain information about the relative position of chromophores. To decrease the computation time, an oligoamide bearing two bithiophene units and a methyl substituent instead of an octyl substituent on the amide nitrogen was used for the calculation (Supplementary Figure S10). Supplementary Figure S11 shows the optimized ground state structure obtained by the Gaussian 09 program at the B3LYP/6-31G level of theory, and two bithiophene chromophores were arranged in a non-parallel manner with the closest distance of approximately 6.9 Å. The above spectroscopic results and theoretical data suggest that poly(*N*-octyl-*m*-benzamide) likely adopts a regular conformation to achieve the π–π interactions of bithiophene chromophores in the repeat unit, and the excited-energy migrates along the polymer chain to transfer to the terminal terthiophene unit. (It should be noted that **M2** has no emission band at approximately 400 nm (Supplementary Figure S8). Therefore, the fluorescence emission of **P1-2-OMe** is derived from not only a terthiophene chromophore at the polymer termini but also a bithiophene chromophore in the repeat unit,
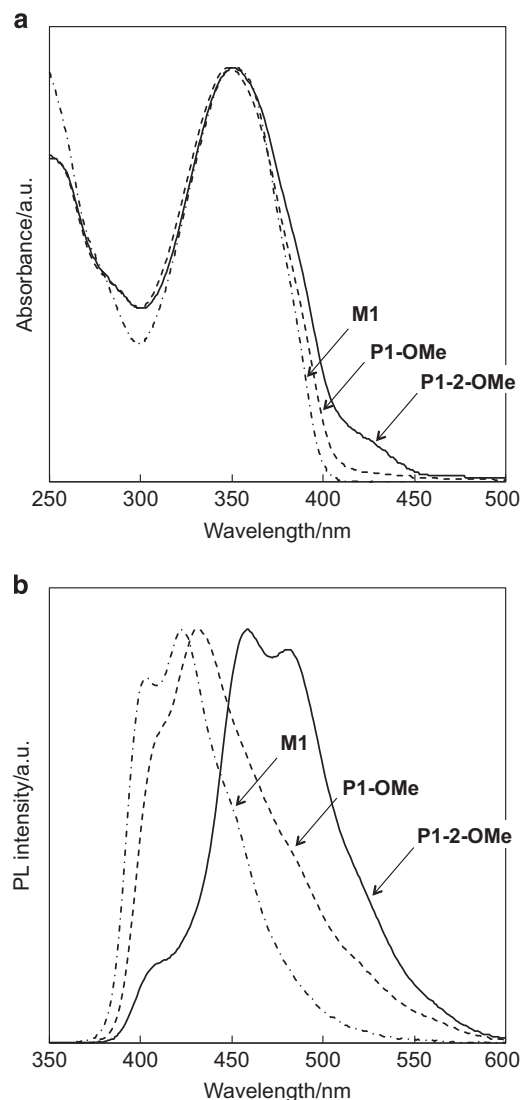
indicating insufficient energy migration and transfer. Additionally, the direct excitation of a terthiophene chromophore is not negligible.)[5]

To understand the energy migration and transfer phenomena in detail, we performed fluorescence lifetime measurements in CHCl$_3$ solutions of the compounds (Figure 6). The model compounds **M1** and **M2** exhibited single-exponential decay curves, and the calculated lifetimes (τ) were 0.27 and 0.34 ns, respectively. The longer lifetime of **M2** with the wide conjugated system is coincident with a previous report.[33] The decay curve of **P1-OMe** was better fitted with a double-exponential function with $\tau = 0.12$ ns and $\tau = 0.90$ ns with weight fractions of 0.91 and 0.09, respectively. This result suggests the presence of two different radiative decay processes from the excited state. Although the quantitative analysis includes some errors due to the low fluorescence quantum yield, the longer lifetime of the minor component is likely attributable to the excimer-like aggregation of chromophores. The shorter lifetime off the major component is a result of the effective trapping of excitation energy.[34] However, the decay curve of **P1-2-OMe** showed a single-exponential fit with a
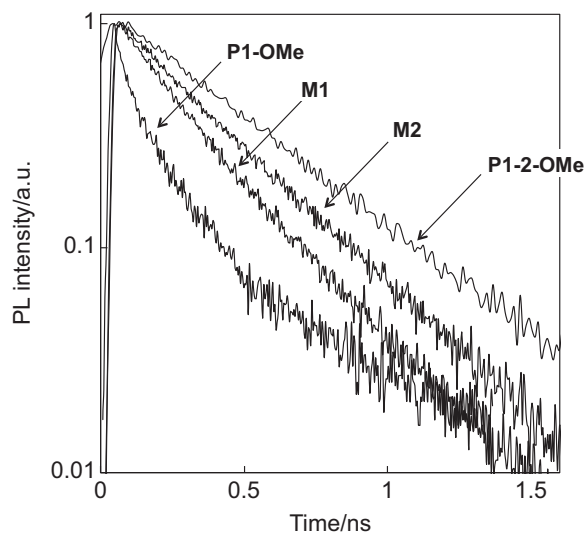
Figure 6 Florescence decay profiles for **M1**, **M2**, **P1-OMe** and **P1-2-OMe** with the excited and monitored wavelengths at their peak maxima.

lifetime of $\tau = 0.44$ ns, indicating selective emission from the terthiophene chromophore at the polymer chain end. In addition, the excitation spectrum of **P1-2-OMe** was measured by monitoring the emission wavelength of the terthiophene chromophore at 456 nm, and the spectrum was similar to the absorption spectrum (Supplementary Figure S9). These steady-state and dynamic fluorescence measurements suggest efficient energy migration between the bithiophene chromophores and fast Förster resonance energy transfer to the terthiophene chromophore in the present system.

CONCLUSIONS

Polymerization of methyl 3-octylaminobenzoate with a bithiophene chromophore at the 5-position of the benzene ring was performed. The molecular weight of **P1-OMe** could be controlled by the monomer/initiator ratio, and a narrow molecular weight distribution and predetermined terminal structure was attained. **P1-2-OMe,** with several bithiophene chromophores in the repeat unit and one terthiophene chromophore at the propagating end, was obtained by the polymer reaction. The low molecular weight model compounds (**M1** and **M2**) were also prepared for comparison. On the basis of the UV-vis absorption and fluorescence emission spectra, fluorescence decay profiles and density functional theory calculation, the π–π interactions between neighboring bithiophene chromophores, and the excited-energy migration along the polymer chain were suggested. Further investigations of the detailed conformation of poly(*N*-alkyl-*m*-benzamide)s and chiral arrangement of chromophores are now in progress.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

1 Dautel, O. J., Wantz, G., Aimairac, R., Flot, D., Hirsch, L., Lere-Porte, J. -P., Parneix, J. P., Serein-Spirau, F., Vignau, L. & Moreau, J. J. E. Nanostructuration of phenylenevinylenediimide-bridged silsesquioxane: from electroluminescent molecular J-aggregates to photoresponsive polymeric H-aggregates. *J. Am. Chem. Soc.* **128**, 4892–4901 (2006).

2 Murphy, C. J., Arkin, M. R., Jenkins, Y., Ghatlia, N. D., Bossman, S. H., Turro, N. J. & Barton, J. K. Long-range photoinduced electron transfer through a DNA helix. *Science* **262**, 1025–1029 (1993).

3 Okahata, Y., Kobayashi, T., Tanaka, K. & Shimomura, M. Anisotropic electric conductivity in an aligned DNA cast film. *J. Am. Chem. Soc.* **120**, 6165–6166 (1998).

4 Fink, H.-W. & Schönenberger, C. Electrical conduction through DNA molecules. *Nature* **398**, 407–410 (1999).

5 Morisaki, Y., Murakami, T. & Chujo, Y. Synthesis and properties of [2.2]Paracyclophane-layered polymers. *Macromolecules* **41**, 5960–5963 (2008).

6 Morisaki, Y., Fernandes, J. A., Wada, N. & Chujo, Y. Synthesis and properties of carbazole-layered polymers. *J. Polym. Sci. Part A Polym. Chem.* **47**, 4279–4288 (2009).

7 Morisaki, Y., Murakami, T., Sawamura, T. & Chujo, Y. [2.2]Paracyclophane-layered polymers end-capped with fluorescence quenchers. *Macromolecules* **42**, 3656–3660 (2009).

8 Morisaki, Y., Sawamura, T. & Chujo, Y. Synthesis of anthracene-stacked oligomers and polymer. *Org. Lett.* **12**, 3188–3191 (2010).

9 Hippius, C., Schlosser, F., Vysotsky, M. O., Böhmer, V. & Würthner, F. Energy transfer in calixarene-based cofacial-positioned perylene bisimide arrays. *J. Am. Chem. Soc.* **128**, 3870–3871 (2006).

10 Hippius, C., van Stokkum, I. H. M., Gsänger, M., Groeneveld, M. M., Williams, R. & Würthner, F. Sequential FRET processes in Calix[4]arene-linked orange-red-green perylene bisimide dye zigzag arrays. *J. Phys. Chem. C* **112**, 2476–2486 (2008).

11 Watanabe, J., Hoshino, T., Nakamura, Y., Sakai, E. & Okamoto, S. Folded H-stacking polymers by conformational control with 2-substituted trimethylene tethers. *Macromolecules* **43**, 6562–6569 (2010).

12 Nomura, R., Moriai, R., Kudo, M., Hoshino, T., Watanabe, J., Funyu, S., Ishitsuka, K. & Okamoto, S. Synthesis and properties of through-space conjugated polymers based on π–π stacked 1,3-biarylpropane tethering units. *J. Polym. Sci. Part A Polym. Chem.* **51**, 3412–3419 (2013).

13 Moriai, R., Naito, Y., Nomura, R., Funyu, S., Ishitsuka, K., Asano, N. & Okamoto, S. Design and synthesis of 2-(1,3-Dialkoxy-2-methylpropan-2-yl)-1,3-diarylpropanes as tethering units for folded H-stacking polymers. *Tetrahedron Lett.* **55**, 2649–2653 (2014).

14 Van Gorp, J. J., Vekemans, J. A. & Meijer, E. W. Facile synthesis of a chiral polymeric helix; folding by intramolecular hydrogen bonding. *Chem. Commun.* 60–61 (2004).

15 Sinkeldam, R. W., van Houtem, M. H., Koeckelberghs, G., Vekemans, J. A. & Meijer, E. W. Synthesis of 3,6-diaminophthalimides for ureidophthalimide-based foldamers. *Org. Lett.* **8**, 383–385 (2006).

16 Sinkeldam, R. W., Hoeben, F. J., Pouderoijen, M. J., Cat, I. D., Zhang, J., Furukawa, S., Feyter, S. D., Vekemans, J. A. J. M. & Meijer, E. W. Chiral alignment of OPV chromophores: exploitation of the ureidophthalimide-based foldamer. *J. Am. Chem. Soc.* **128**, 16113–16121 (2006).

17 Vanormelingen, W., Van den Bergh, K., Verbiest, T. & Koeckelberghs, G. Conformational transitions in chiral, gallic acid-functionalized poly(dithienopyrrole): a comparative UV-vis and CD study. *Macromolecules* **41**, 5582–5589 (2008).

18 Vanormelingen, W., Pandey, L., Van der Auweraer, M., Verbiest, T. & Koeckelberghs, G. Steering the conformation and chiroptical properties of poly(dithienopyrrole)s substituted with chiral OPV side chains. *Macromolecules* **43**, 2157–2168 (2010).

19 Nakano, T., Takewaki, K., Yade, T. & Okamoto, Y. Dibenzofulvene, a 1,1-diphenylethylene analogue, gives a π-stacked polymer by anionic, free-radical, and cationic catalysts. *J. Am. Chem. Soc.* **123**, 9182–9183 (2001).

20 Nakano, T. & Yade, T. Synthesis, structure, and photophysical and electrochemical properties of a π-stacked polymer. *J. Am. Chem. Soc.* **125**, 15474–15484 (2003).

21 Nakano, T., Yade, T., Fukuda, Y., Yamaguchi, T. & Okumura, S. Free-radical polymerization of dibenzofulvene leading to a π-stacked polymer: structure and properties of the polymer and proposed reaction mechanism. *Macromolecules* **38**, 8140–8148 (2005).

22 Yade, T. & Nakano, T. Anionic polymerization of 2,7-Di-t-butyldibenzofulvene: synthesis, structure, and photophysical properties of the oligomers with a π-stacked conformation. *J. Polym. Sci. Part A Polym. Chem.* **44**, 561–572 (2006).

23 Nakano, T., Yade, T., Yokoyama, M. & Nagayama, N. Charge transport in a π-stacked poly(dibenzofulvene) film. *Chem. Lett.* **33**, 296–297 (2004).

24 Coropceanu, V., Nakano, T., Gruhn, N. E., Kwon, O., Yade, T., Katsukawa, K. & Brédas, J.-L. Probing charge transport in π-stacked fluorene-based systems. *J. Phys. Chem. B* **110**, 9482–9487 (2006).

25 Nobuke, K., Yamakado, R. & Takagi, K. Polycondensation of 4-octylaminobenzoic acid esters having bithiophene at 3-position and optical properties of polymer. *Kobunshi Ronbunshu* **68**, 33–38 (2011).

26 Takagi, K., Nobuke, K., Nishikawa, Y. & Yamakado, R. Synthesis and optical properties of poly(*p*-benzamide)s bearing oligothiophene on amide nitrogen atom through alkylene spacer. *Polym. J.* **45**, 1171–1176 (2013).

27 Yamazaki, K., Yokoyama, A. & Yokozawa, T. Solvent and temperature effect on chiral conformation of poly(*m*-benzamide)s. *Macromolecules* **39**, 2432–2434 (2006).

28 Nelson, J. C., Saven, J. G., Moore, J. S. & Wolynes, P. G. Solvophobically driven folding of nonbiological oligomers. *Science* **277**, 1793–1796 (1997).

29 Gong, B. Crescent oligoamides: from acyclic "macrocycles" to folding nanotubes. *Chem. Eur. J.* **7**, 4336–4342 (2001).

30 Huc, I. Aromatic oligoamide foldamers. *Eur. J. Org. Chem.* 17–29 (2004).

31 Takagi, K., Sugimoto, S., Yamakado, R. & Nobuke, K. Self-assembly of oligothiophene chromophores by *m*-Calix[3]amide scaffold. *J. Org. Chem.* **76**, 2471–2478 (2011).

32 Ohishi, T., Sugi, R., Yokoyama, A. & Yokozawa, T. A variety of poly(m-benzamide)s with low polydispersities from inductive effect-assisted chain-growth polycondensation. *J. Polym. Sci. Part A Polym. Chem.* **44**, 4990–5003 (2006).

33 Becker, R. S., Seixas de Melo, J., Macanita, A. L. & Elisei, F. Comprehensive evaluation of the absorption, photophysical, energy transfer, structural, and theoretical properties of r-oligothiophenes with one to seven rings. *J. Phys. Chem.* **100**, 18683–18685 (1996).

34 Synak, A., Grobelna, B., Kułak, L., Lewkowicz, A. & Bojarski, P. Local dye concentration and spectroscopic properties of monomer–aggregate systems in hybrid porous nano-layers. *J. Phys. Chem. C* **119**, 14419–14426 (2015).

Supplementary Information accompanies the paper on Polymer Journal website (http://www.nature.com/pj)