Macromolecules **2008**, *41*, 7933−7937 **7933**

Blue-Emitting Poly(2,7-pyrenylene)s: Synthesis and Optical Properties

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Received July 30, 2008; Revised Manuscript Received August 29, 2008

ABSTRACT: The first 2,7-linked conjugated polypyrene tethering four aryl groups has been synthesized, and the photophysical properties of the polymer have been characterized. Due to the unique substitution with bulky aryl groups at the 4,5,9,10-positions of pyrene, the polymer although comprising large π-units is readily soluble in common organic solvents. The polymer has a blue fluorescence in solution with an emission band maximum at $\lambda = 429$ nm, fulfilling the requirements for a blue-emitting polymer. To a first approximation, this can be attributed to electronically decoupled pyrene subunits due to the nodal properties of their frontier orbitals. Furthermore, in solution the intriguing blue fluorescence is combined with solvent-dependent features, which could be used as a probe for local solvent polarity. Finally, in the solid state, the red-shifted emission of the polymer could be strongly reduced by blending with a nonconjugated polymer such as polystyrene.

Conjugated polymers have received a great deal of interest due to their optical and electrical properties.[1] In the family of conjugated polymers, poly-*p*-phenylene (PPP) and its derivatives have HOMO−LUMO energy gaps required for obtaining blue emission, which is the most difficult part among the red, green, and blue (RGB) organic emitters. To establish both solubility and desirable emission bands, we and others have investigated poly(tetrahydropyrenylene) (PTHP),[2] polyfluorene (PF, **P1**; Figure 1),[3] poly(2,8-indenofluorene) (PIF),[4] ladder-type PPP (LPPP),[5] and poly(2,7- or 3,6-phenanthrylene)s (**P2**; Figure 1)[6] as attempts to introduce solubilizing side chains without hampering the conjugation within the aromatic π-system. Although **P1**, PIF, and LPPP exhibit remarkably high fluorescence intensities, under certain circumstances they develop an unwanted long-wavelength emission; this has recently been attributed to formation of keto defects in the polymers.[7]

Pyrene has been intensively used as a blue-emitting fluorescence probe for biological analysis and is well characterized by a long excited-state lifetime and distinct solvatochromic phenomena.[8] Furthermore, characteristic excimer formation has been detected in concentrated solutions and also in the solid state.[9] We have shown that oligopyrenes linked at their 2,7-positions, to a first approximation, possess electronically decoupled pyrene subunits due to the nodal properties of their frontier orbitals.[10] This insight strongly encouraged us to construct 2,7-linked polypyrenylenes because such polymers should hold promise both as blue light emitters and as a probes for local polarity.

Herein, we describe the synthesis and photophysical properties of the first 2,7-linked conjugated polypyrenylene, **P3** (Figure 1), tethering four aryl groups. Among the polymers which we introduce, **P3** shows an intriguing blue and solvent-dependent fluorescence in solution and strong red-shifted emission in films.

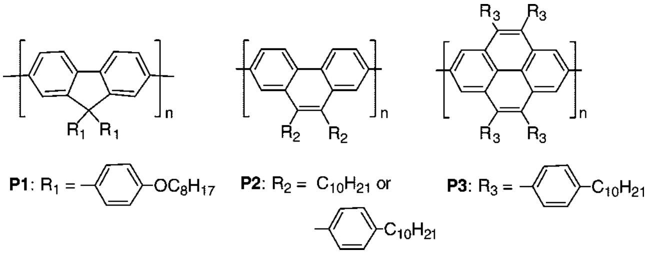

Figure 1. Chemical structures of "polyfluorene", polyphenanthrylene, and polypyrenylene.

The synthesis of the 2,7-dichloropyrene derivative **1** with peripheral phenyl groups is shown in Scheme 1. 4-Chloro-2,6-dimethyliodobenzene (**4**) was obtained by Sandmeyer reaction with **3**.[11] Oxidation of the methyl groups resulted in a dicarboxylic acid derivative, **5**.[12] Subsequently, 5-chloro-2-iodo-3-(4″-dodecylphenyl)-4′-decylbenzophenone (**6**) was obtained by treatment of **5** with $SOCl_2$ followed by Friedel−Crafts arylation with 1-phenyldodecane. After Ullmann coupling of **6**, the resulting 4,4′-dichloro-2,2′,6,6′-tetrakis(*p*-decylphenyl)-1,1′-biphenyl (**7**) was subjected to cyclization using tricyclohexyltin sulfide and trichloroborane to afford the 2,7-dichloropyrene **1**.[13] The 4,5,9,10-tetraphenylpyrene **2** was synthesized as a model compound for the polymer by a similar scheme (see Scheme S1, Supporting Information). A single crystal of **2** was grown by slow evaporation of a $CHCl_3$ solution of **2** at room temperature. The X-ray structure analysis revealed that the $\pi-\pi$ distance between the pyrene planes is 0.51 nm; thus, direct π-stacking is prevented. This closest distance in the solid state is thus too large to allow for the formation of excimers (Figure 2). Expectedly, this hindrance between the pyrenes is due to the sterically demanding phenyl groups, which possess a dihedral angle of 84° against the pyrene plane. These results encouraged us to synthesize the 2,7-linked polypyrene, which was then found to have good solubility in common organic solvents even though it contains relatively large fluorophores.

The polymerization of monomer **1** was carried out in a Yamamoto coupling with a Ni(0) catalyst.[14] Unexpectedly, when the polymerization was conducted under standard conditions, the product contained only low-molecular-weight compound **P3a**. Gel permeation chromatography (GPC) analysis (THF, PPP standards) indicated that the sample consisted mainly of a dimer and a trimer (with a number-average molar mass $M_n = 2600$ g/mol and a weight-average molar mass $M_w = 3100$ g/mol, PD $= 1.2$). When the analogous Yamamoto polycondensation was performed utilizing microwave heating, however, a high-molecular weight product, **P3b**, was obtained.[15] After precipitation in a mixture of concentrated HCl and methanol (1:1) and

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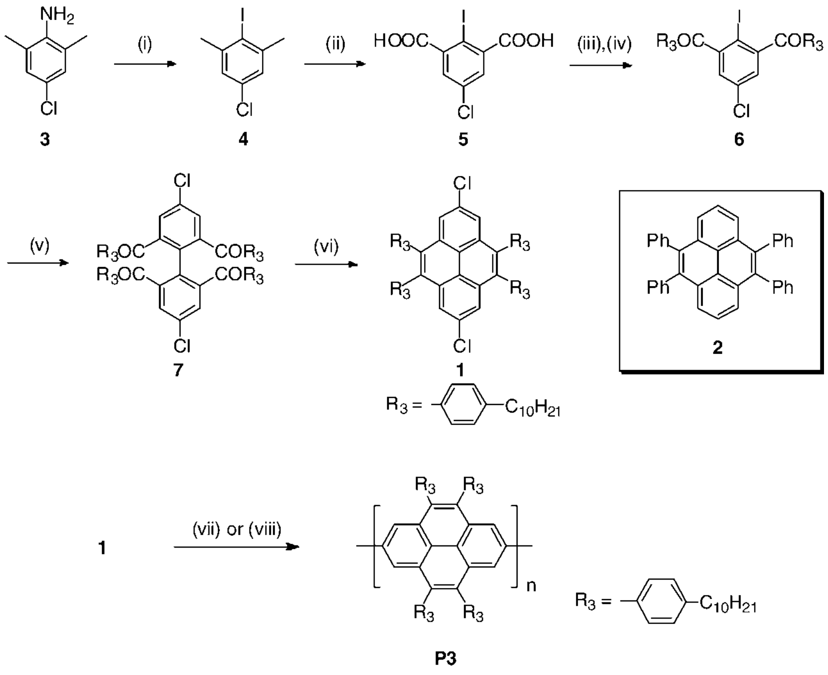
10.1021/ma8017316 CCC: $40.75

Scheme 1. Synthetic Scheme for Monomer 1 and Polypyrenes P3[a]



[a] Reagents and conditions: (i) $NaNO_2$, concentrated HCl, KI, at room temperature, 68%; (ii) $KMnO_4$, H_2O, pyridine, at 115 °C, 78%; (iii) $SOCl_2$ at 80 °C; (iv) $AlCl_3$, 1-$PhC_{10}H_{21}$ in CH_2Cl_2 at 0 °C, 27% for two steps; (v) Cu powder, DMF at 110 °C, 42%; (vi) 1 M BCl_3 in CH_2Cl_2, bis(tricyclohexyltin) sulfide, at room temperature, 23%; (vii) for **P3a**, Ni(cod)$_2$, cyclooctadiene, 2,2′-bipyridyl in toluene and DMF at 80 °C, 42%; (viii) for **P3b**, Ni(cod)$_2$, cyclooctadiene, 2,2′-bipyridyl in toluene and DMF at 80 °C utilizing microwave heating (80 W, 60 min), 66%.

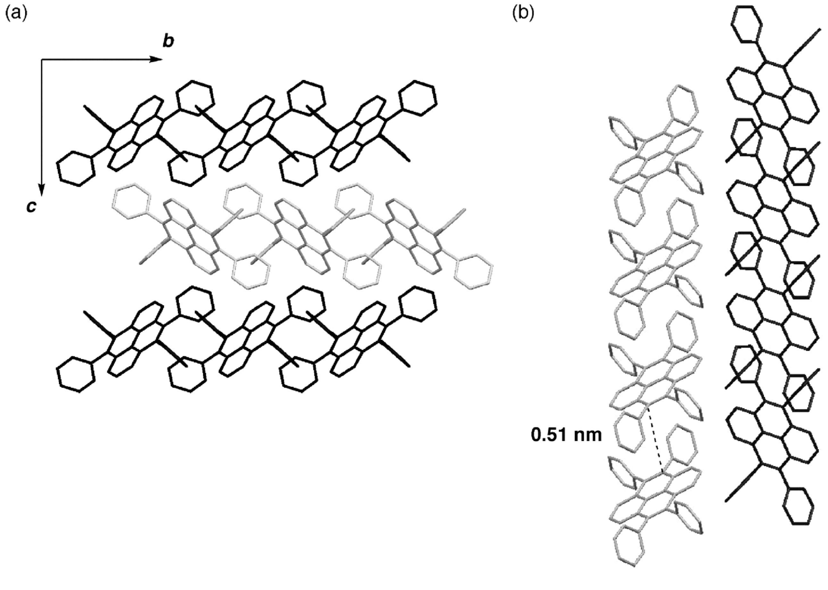


Figure 2. Single-crystal structure of **2**: (a) crystal structure viewed along the *a* axis; (b) the $\pi-\pi$ distance of the pyrene planes is 0.51 nm, and the dihedral angle between pyrene and the peripheral phenyl groups is 84°.

subsequent removal of the low-molecular-weight species by Soxhlet extraction with acetone, GPC measurements of the new macromolecule showed M_n = 21 800 g/mol, M_w = 39 000 g/mol, and PD = 1.7; the resultant polymer corresponds to a molecular structure of approximately 20 repeat units. Even though their main chains are comprised of a large π-disk of 16 aromatic carbons, both **P3a** and **P3b** exhibit good solubilities in common organic solvents (e.g., THF, toluene, and chlorinated hydrocarbons), enabling us to characterize the polymer by ^{1}H and ^{13}C NMR spectroscopy and also to investigate the optical properties in solution.[16]

The UV−vis absorption and fluorescence spectra of model compound **2** and **P3b** in 1,2-dichlorobenzene are shown in Figure 3. Similar to the parent pyrene, these pyrenes with four aryl groups have strong $S_0 \rightarrow S_2$ transition in the UV region.[17] The forbidden $S_0 \rightarrow S_1$ transition around λ = 400 nm is very weak.[18] Compared to the absorption spectrum of **2**, those of **P3a** and **P3b** exhibit similar features due to vibronic coupling and their absorption maxima are bathochromically shifted by 9 and 20 nm, respectively (see Table 1). Judging from the small red shift of the absorption maxima, the effective conjugation length of the polymer seems to be small compared to that of

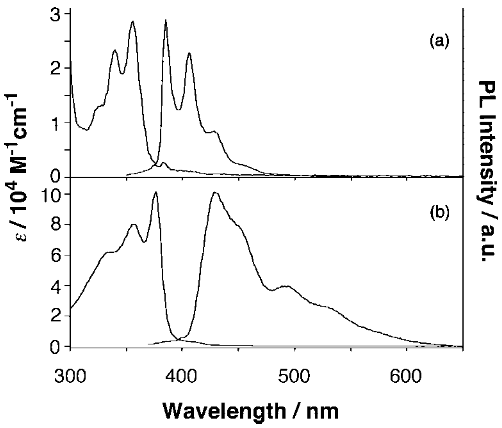


Figure 3. Absorption and fluorescence spectra of (a) **2** ($\lambda_{ex} = 340$ nm) and (b) **P3b** ($\lambda_{ex} = 325$ nm) in 1,2-DCB (1,2-dichlorobenzene). The molecular extinction coefficient of **P3b** was evaluated by counting the repeating unit.

other conjugated polymers.[19] These results support our expectation that the conjugation along the main chain is hampered by the connection of the pyrenes through the nodal planes of the frontier orbitals, leading to partial electronic decoupling of the repeating units.

P3b shows a blue fluorescence in solution, with an emission maximum at $\lambda = 429$ nm, thus fulfilling well the requirements for a blue-emitting polymer. However, unlike the other PPP-type conjugated polymers,[1−6] the fluorescence spectra of **P3** exhibit a remarkable long-wavelength tailing as well as additional emission bands with maxima at $\lambda = 493$ and 530 nm.

Thus far, different models have been proposed to explain the origin of the green (red-shifted in comparison with the singlet emission of the corresponding monomer unit) emission band for the blue conjugated polymers. However, none of these models have yet conclusively resolved the exact nature of these green emissions. For example, in the case of polyfluorene, some research groups suggested that the low-energy emission band is attributed to the formation of aggregates and/or intermolecular excimers.[20] On the contrary, the emission from isolated chemical defects (such as fluorenone) on the polyfluorene chain, rather than intermolecular aggregates or excimers, has been proposed as a possible reason for the appearance of the green emission band.[7b,21] These fluorenone defects could be formed either during polymerization or later on during thermal oxidation or photo-oxidation of polyfluorene films.[7b,22] Thus, within this context, the low-energy green emission band is a consequence of exciton trapping[23] on fluorenone sites that is then followed by a charge-transfer $\pi-\pi^*$ radiative transition[24] to the ground state. Indeed, the charge-transfer nature of this emission has already been experimentally confirmed because this emission of polyfluorene was found to exhibit solvatochromic effects.[25] Thermally induced cross-linking reactions have also been identified as the origin for the low-energy emission band.[26] Therefore, following this aforementioned strategy described in the literature,[20−26] we tried to recognize and verify the most probable explanation for the substantially red-shifted band in the case of **P3**.

At first, the bathochromically shifted bands were assessed by the measured concentration dependence of the fluorescence. The fluorescence spectral shape of **P3b** did not change even under very high dilutions such as 10^{-8} M per monomer unit, indicating that the polymers do not form interchain aggregates in solution (see Figure S2, Supporting Information). Furthermore, the concentration dependence of the fluorescence of model compound **2** ([**2**] from 0.5 mM to 1.0 μM in cyclohexane) revealed that the peripheral aryl groups of the pyrene very effectively prevent aggregation of the fluorophore cores.[27]

In principle, a red shift of the emission bands could also be induced by intramolecular charge transfer, which would be evidenced by solvatochromic shifts of the emission maxima.[29] However, for **P3b** no solvent dependence of the position of the fluorescence maxima of the polymer through the use of solvents of different polarities could be found. Furthermore, only changes in the relative intensities of these fluorescence maxima were observed (Figure 4a). These facts together indicate that the red-shifted emission bands at $\lambda = 490-530$ nm cannot be ascribed to charge transfer in the polymer chain. Therefore, the fluorescence behavior was studied by time-resolved measurements in more depth.

Thereby, the fluorescence lifetimes of the local bands around $\lambda = 440$, 480, and 525 nm from the fluorescence spectrum of **P3b** in MTHF (77 K) were measured, yielding 4.9, 6.0, and 7.5 ns, respectively (Figure S4f, Supporting Information). Since the emission maxima of **P3b** in toluene solution at room temperature showed fluorescence lifetimes in the same order as in frozen solution, this result indicates that the emissions around $\lambda = 493$ and 530 nm are derived from dissolved single chains (Table 1 and Figure S4b, Supporting Information).

However, an intramolecular energy redistribution in the single chain might take place as the lifetimes of shorter wavelength bands are lower than those of the longer wavelength bands.[30] Combining all the results discussed above, one can conclude that the red-shifted broad emission bands are not caused by aggregation, but by *intramolecular* energy redistribution between the vibrational manifold of the single polymer chain.[31,32]

The blue fluorescence of **P3b** in solution shown in Figure 3 suggests to investigate the properties of the polymers in thin films. The films were prepared by spin-coating on glass substrates from **P3b** in toluene ([repeating unit] = 1.9×10^{-6} M). The thicknesses of the thin films were 80−160 nm. The measurements of the optical properties of the studied materials were conducted in a vacuum chamber (residual dynamic pressure of 10^{-5} mbar), and time-resolved spectra were obtained by a streak camera.

The fluorescence of the thin films was of a green color, considerably different from the predominantly blue fluorescence observed in solution. The intensity ratio between the localized emission maxima in the fluorescence spectra of the thin film samples was drastically changed when going to the solid state: As shown in Figure S4c (see I and II), Supporting Information, the intensity of the blue part of the emission spectrum (i.e., the emission maxima at $\lambda = 429$ and 458 nm) decreased in comparison with that of the other bands from the longer wavelength region. Correspondingly, the lifetime of these two emissions (I and II) significantly shortened, more than 4-fold (see Figure S4d, Supporting Information), in comparison with those in solution. This result can be explained by further increased energy redistribution within the polymer chains with some aggregation between polymer chains, as a broad shoulder in the fluorescence spectrum of all the films emerges between 550 and 600 nm.[6]

In an attempt to recover in the solid state at least part of the relative intensity of the blue fluorescence found in solution, films of blends containing the conjugated polymer **P3b** and polystyrene (PS; M_n = 21 000 g/mol, PD = 1.4, PS standard) were

Table 1. Absorption and Fluorescence Data of 2, P3a, and P3b in 1,2-DCB

compd	λ_{abs}/nm (ε/M^{-1} cm^{-1})	$\lambda_{fl}{}^{a}$/nm	Φ_f	HOMO^e/eV	LUMO^e/eV
2	325 (13 000) 340 (23 000) 356 (62 000)	385, 406, 428 (454)	0.22^b	−5.75	−2.62
P3a	302 (46 000) 347 (27 000) 365 (30 000)	425 (450), 492, 529	0.13^b	−5.66	−3.05
P3b	334 (62 000) 356 (81 000) 376 (100 000)	429 (449), 493 (530)	0.09^c	−5.66	−3.39
film of **P3b**^{d}	333 355 374	442, 495, 522			

[a] The values in parentheses indicate the shoulder bands. [b] Fluorescence quantum yield, determined in THF by using 9,10-diphenylanthracene ($\Phi_f = 0.91$ in EtOH). [c] The relative fluorescence quantum yield was determined when **P1** was used as a standard. [d] The film was prepared by spin-coating from the $CHCl_3$ solution (7 g/mL). [e] Estimated from a combination of CV data and the onset wavelength of optical absorption in CH_2Cl_2.

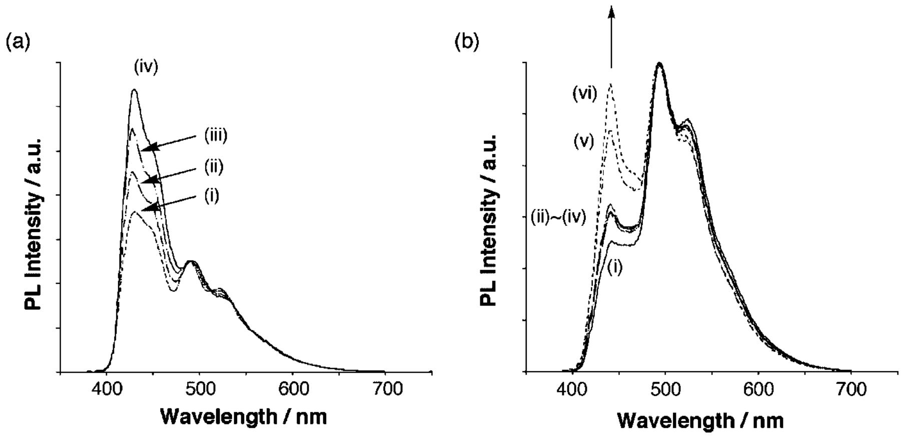


Figure 4. (a) Solvent dependence of fluorescence spectra of **P3b**, $\lambda_{ex} = 375$ nm, [unit] = 1.9×10^{-6} M. For clarity, the spectra were normalized regarding the amplitude at 490 nm. Arrows indicate the corresponding spectrum taken in different solvents. The subsequent dielectric constants are given in parentheses in the following: (i) cyclohexane (2.0), (ii) THF (7.6), (iii) $CHCl_3$ (4.8), (iv) 1,2-DCB (9.9).[28] (b) Fluorescence spectral change induced by blending **P3b** with PS, $\lambda_{ex} = 371$ nm: (i) 0 wt %, (ii) 50 wt %, (iii) 67 wt %, (iv) 80 wt %, (v) 91 wt %, and (vi) 95 wt % PS to **P3b**. For clarity, the spectra were normalized to the emission peak at 494 nm.

prepared.[33] The monotonic increase of the relative concentration of PS led to a significant increase of the blue part of the fluorescence emission of **P3b** (Figure 4b, I−VI). At 95 wt % PS, the local emission maxima at $\lambda = 429$ and 458 nm were twice as intense as the same bands in pure **P3b** film spectra (Figure 4b, VI). Nevertheless, the most intense band remained the one peaking at 494 nm. These results confirm previous reports[33,34] that polystyrene could efficiently suppress aggregation of conjugated polymers in films, even though in our case of the **P3b** polymer the green emission still dominates.

It is known that the solvent-dependent fluorescence of pyrene is extensively used for probing local polarity (the Ham effect).[17] The relative emission intensity derived from the highest energy level of the pyrene is dependent upon the solvent polarity. The solvent dependence of the fluorescence spectra of **P3b** indicates that the apparent increase of the emission intensity at 430 nm was observed with an increase of the polarity of the solvent (Figure 4a). Thus, the relative fluorescence intensity at 430 nm in 1,2-DCB (where the dielectric constant is 9.9) was about 1.8 times higher than that in cyclohexane (where the dielectric constant is 2.0). On the contrary, **P1** and **P2** do not show a similar solvatochromic effect. This property of **P3b** could have applications in materials processing, for example, as a sensor for probing the polarity of the surrounding media.[17]

In conclusion, 2,7-linked conjugated tetraphenylpyrene-based polymers have been synthesized by Yamamoto polycondensation. Due to the unique substitution with bulky alkylaryl units at the 4,5,9,10-positions of pyrene, the polymer although composed of large π-units is soluble in common organic solvents. The polymer shows a blue fluorescence in solution with an emission band maximum at $\lambda = 429$ nm, fulfilling the requirements for a blue-emitting organic semiconductor. The polymer has bathochromically shifted emission bands, a phenomenon which becomes more pronounced in the solid state. The red-shifted broad emission bands observed at the polymer fluorescence in solution are not caused by aggregation, but by *intramolecular* energy redistribution between the vibrational manifold of the single polymer chain. The additional red-shifted emission of the polymer in the solid state could be strongly reduced by blending with a nonconjugated polymer such as the polystyrene. Finally, in solution the polymer possesses a fluorescence with solvent-dependent features and could be used for probing local solvent polarity.

Acknowledgment. We thank Dr. H. Benten for fruitful discussions and advice. We also thank Dr. V. Enkelmann for the single-crystal X-ray structural analysis of compound **2**. The Deutsche Forschungsgemeinschft is gratefully acknowledged for financial assistance. Postdoctoral support for S.-i.K. was provided by a JSPS Research Fellowship for Young Scientists. M.R. thanks the DAAD for a Ph.D. scholarship.

Supporting Information Available: Text giving detailed experimental procedures for the syntheses of all the new materials, ^{1}H NMR spectra of **1** and **2**, solvent dependencies of the fluorescence of **P3**, fluorescence spectra of pyrene and **2** in concentrated solution, concentration and fluorescence of decay data of **P3b** in solution and a film, and excitation spectra and temperature-dependent fluorescence of **P3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(32) Excitation spectra excited at different wavelengths, 429, 493, and 527 nm, indicated that all of the shapes of the excitation spectra are similar to each other and to that of the absorption spectrum (Figure S5a, Supporting Information). Moreover, in general, if aggregation occurs, the fluorescence of the chromophore is red-shifted and the fluorescence intensity of the longer wavelength decreases with increasing temperature. However, in the case of the polypyrene, when the temperature increased, the fluorescence did not show any bathochromic shift, but the intensity at 440 nm decreased compared to that at 550 nm (Figure S5b, Supporting Information). Therefore, these results indicate the fluorescence we discussed here is from a single species.

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MA8017316