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### COMMUNICATION

# Solvent-dependent fluorescence and circular dichroism properties of poly(quinoxaline-2,3-diyl)s bearing pyrene pendants

Yuuya Nagata,<sup>a</sup> Tsuyoshi Nishikawa<sup>a</sup> and Michinori Suginome<sup>\*ab</sup>

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Poly(quinoxaline-2,3-diyl)s bearing pyrene pendants exhibited solvent-dependent changes of the fluorescence color (blue and green) and the screw-sense selectivity (left-handed and racemic) in chloroform and 1,1,1-trichloroethane, 10 respectively.

Reversible and efficient control of the screw sense of helical polymers has attracted considerable interest, because it leads to the exploration of new chiral functional materials.<sup>1-6</sup> We have recently reported that poly(quinoxaline-2,3-diyl)s bearing chiral <sup>15</sup> side chains adopt pure right- and left-handed screw senses in chloroform and 1,1,2-trichloroethane, respectively.<sup>7</sup> We also reported a new class of polymer-based chiral ligand PQXphos;<sup>8</sup> its enantioselectivity could be perfectly controlled by solvent-dependent helix inversion of its backbone of poly(quinoxaline-<sup>20</sup> 2,3-diyl).<sup>9, 10</sup> Although we suggested the conformational change of chiral side chains as the mechanism of the helix inversion,<sup>7</sup> the details were not clear. We have expanded much effort to find evidence for the proposal, concluding that any conformational probes should be introduced to the polymer side chains.

- <sup>25</sup> Pyrene has been widely used as a probe to determine conformations and conformational changes of biomolecules,<sup>11, 12</sup> molecular switches,<sup>13-15</sup> and macromolecules,<sup>16-18</sup> because an excimer emission of pyrene reflects the presence of another pyrene unit in spatial proximity. In general, when two pyrene
- <sup>30</sup> rings are located within a few angstroms of each other, they exhibit a broad, unstructured band at longer wavelengths around 500 nm (green color) as an excimer emission.<sup>19</sup> In this Communication, poly(quinoxaline-2,3-diyl)s bearing pyrene pendants were prepared to obtain information about the
- <sup>35</sup> conformation of the side chain. We observed a fluorescent color change between chloroform and 1,1,1-trichloroethane (1,1,1-TCE), which may originate from adjacent conformation of two pyrene rings on the same monomer unit. This conformational

preference leads to the induction of a single screw sense, which can be detected by fluorescence spectroscopy. We have also established a quick and simple method for screening solvents for efficient induction of single-handed helices.



<sup>&</sup>lt;sup>40</sup> <sup>a</sup> Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan. E-mail: suginome@sbchem.kyoto-u.ac.jp Fax: +81-75-383-2723; Tel: +81-75-383-2722;

Pax. + 01 - 7 - 503 - 2723, 101. + 01 - 7 - 503 - 2722,

<sup>&</sup>lt;sup>45</sup> JST, CREST (Creation of Next-Generation Nanosystems through Process Integration), Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan.

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<sup>&</sup>lt;sup>60</sup> Poly(quinoxaline-2,3-diyl)s bearing pyrene pendants **1–3** were synthesized by post-polymerization functionalization of the corresponding silyl-protected polymer (Scheme 1). All conversions proceeded quantitatively, as confirmed by <sup>1</sup>H NMR. All the polymers yielded in this experiments showed good <sup>65</sup> solubility in organic solvents such as toluene, THF, CHCl<sub>3</sub>, and 1,1,1-TCE. The number-average molecular weights ( $M_n$ ) and polydispersity indexes ( $M_w/M_n$ ) determined by size exclusion chromatography using polystyrene standards suggested that this polymerization proceeded in a living fashion. The corresponding <sup>70</sup> model compounds **4–6** were also prepared for comparison.



**Fig. 1** CD and FL spectra of polymer **1** (a: CD, b: FL) and model **6** (c: CD, d: FL) in CHCl<sub>3</sub> and in 1,1,1-TCE.



5 Fig. 2 CD and FL spectra of polymer 2 (a: CD, b: FL) and polymer 3 (c: CD, d: FL) in CHCl<sub>3</sub> and in 1,1,1-TCE.

To evaluate the relationship between fluorescence properties and the screw-sense selectivities, circular dichroism (CD) spectra and fluorescence (FL) spectra were measured in CHCl<sub>3</sub> and 1,1,1-<sup>10</sup> TCE. Polymer **1** showed a clear negative Cotton effect in CHCl<sub>3</sub> (Fig. 1a), suggesting that polymer **1** adopted a left-handed helical backbone. As none of model compounds **4–6** showed CD signals in the observed region, pyrene units may have little influence on the CD spectra of polymer **1**. Polymer **1** exhibited an intense <sup>15</sup> green emission at 514 nm in CHCl<sub>3</sub>, which originated from the pyrene excimer. On the other hand, CD signals and the excimer emission of polymer **1** were dramatically suppressed in 1,1,1-TCE. FL measurements of model **6** gave almost the same spectra in CHCl<sub>3</sub> and in 1,1,1-TCE as shown in Fig. 1d, suggesting the <sup>20</sup> changes in the fluorescence spectra of polymer **1** rely on the existence of the polymer main chain.

CD and FL measurements of polymer **2** bearing additional chiral side chains were also performed. As shown in Fig. 2a, polymer **2** adopted left- and right-handed screw senses in <sup>25</sup> chloroform and 1,1,1-TCE, respectively. This helix inversion was caused by the chiral side chains on the pyrene-free monomer units. The FL spectra of polymer **2** were almost identical to those of polymer **1**, indicating that the conformation of the two pyrene

units on the quinoxaline ring was not affected by the screw-sense <sup>30</sup> of the polymer backbone. This means that the solvent-dependent fluorescence color change reflected a local conformation of the pyrene pendants. In Figs. 2c and 2d, the CD and FL spectra of polymer **3** are shown. Because polymer **3** possessed no chiral centers, no CD signals were observed. However, the observed <sup>35</sup> solvent-dependent fluorescent color change was the same as for polymers **1** and **2**.

Two side chains on the same quinoxaline ring have opposed, 'up-and-down' arrangements because of steric hindrance. These enantiomeric conformations are defined as  $\delta$ - and  $\lambda$ -forms<sup>20</sup> as <sup>40</sup> shown in Fig. 3. Considering these conformers, possible conformations of polymer **3** are shown in Fig. 4 using heptaquinoxaline bearing two pyrene groups on the central quinoxaline rings. Note that the  $\lambda$ -form and *M*-helix state is

identical to the  $\delta$ -form and *P*-helix state, because polymer **3** has <sup>45</sup> no chiral centers. However, **A'** and **B'** could be distinguished because of their diastereomeric relationship. Polymer **3** might adopt conformer **A** in CHCl<sub>3</sub> and conformer **B** in 1,1,1-TCE.



<sup>50</sup> Fig. 3 Conformations of two side chains on a same quinoxaline ring ( $\delta$  and  $\lambda$ -form). a...a indicates the plane of the quinoxaline ring, and b-b represents the line passing through the two side chains, R.



Fig. 4 Possible conformations of polymer 3. Only seven quinoxaline units, 55 of which side chains except for those on the central quinoxaline ring are omitted for clarity, are shown.

According to the results of the CD and FL measurements, possible conformations of polymers 1 and 2 can be suggested. Figure 5 shows representative conformers A–D, which have a 60 diastereomeric relationship because of the chiral centers on the side chains. Polymer 1 showed an intense excimer emission and *M*-helical structure in CHCl<sub>3</sub>, and adopted conformer A in CHCl<sub>3</sub>. In contrast, in 1,1,1-TCE, polymer 1 did not show good selectivity among conformers A–D because the CD signals and 65 the excimer emission were suppressed. Polymer 2 showed a lefthanded screw sense with intense excimer emission in chloroform and right-handed screw sense with weak excimer emission in 1,1,1-TCE. Thus, polymer 2 adopted conformer A in CHCl<sub>3</sub> and conformer D in 1,1,1-TCE. These observations of the solvent-70 dependent fluorescent color changes conformed that the conformational change of the side chain certainly occurred.

Although this color change was not directly dependent on the screw-sense selectivity of the polymer main chain, it could reflect a local conformation of the chiral side chain modified by the <sup>75</sup> pyrene unit. Therefore, as far as the chiral pyrene units were the sole source of chirality, the screw-sense selectivity should be related to the intensity of the excimer emission. We performed a fluorescence screening of solvents for efficient induction of a single-handed helical backbone. Polymer **1** was dissolved in

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**Fig. 5** Possible conformations of polymers **1** and **2**. Only seven quinoxaline units, of which side chains except for those on the central quinoxaline ring are omitted for clarity, are shown.



Fig. 6 (a) Photograph of polymer 1 dissolved in various solvents under UV irradiation (365 nm). (b) Relative intensity of excimer emission of polymer 1 dissolved in various solvents (519 nm). Fluorescence intensities were normalized by UV absorbance at 371 nm. (c)
<sup>10</sup> Representative CD spectra of polymer 1 dissolved in various solvents.

various solvents and observed under 365 nm UV light. As shown in Fig. 6a, polymer **1** showed intense excimer emissions in  $CHCl_3$ and 1,1,2,2-tetrachloroethane. The relative intensities of the excimer emissions in various solvents are shown in Fig. 6b. The

- <sup>15</sup> differences in the intensities of the excimer emissions were recognizable by the naked eye. Selected CD spectra are shown in Fig 6c (see ESI for other spectra). While almost all solvents gave an almost racemic helical backbone, only CHCl<sub>3</sub> and 1,1,2,2tetrachloroethane could induce single-handed helical backbones.
- <sup>20</sup> Interestingly, polymer **1** adopted the *P*-helical form in toluene, probably because of  $\pi$ - $\pi$  interaction between the toluene and pyrene rings.

#### Conclusions

In summary, we have synthesized a series of poly(quinoxaline-<sup>25</sup> 2,3-diyl)s bearing pyrene pendants to reveal the conformational changes of their side chains. Polymer **1**, which has pyrenemodified chiral side chains and achiral side chains, exhibited intense excimer emission in CHCl<sub>3</sub> and adopted the *M*-helical form. However, the CD signals and the excimer emission of <sup>30</sup> polymer **1** were suppressed in 1,1,1-trichloroethane. Polymers **2** (pyrene-modified chiral side chains and chiral side chains) and **3** (pyrene-modified achiral side chains and achiral side chains) showed similar solvent-dependent fluorescence changes in CHCl<sub>3</sub> and 1,1,1-trichloroethane. Based on these results, we showed that

<sup>35</sup> the helix and fluorescence switches depend on solvent-induced conformational changes of the chiral side chains. Finally, we have established a quick and simple method for screening solvents for the efficient induction of a single-handed helical backbone. In addition, 1,1,2,2-tetrachloroethane was found to be <sup>40</sup> an efficient solvent for the asymmetric helix induction. Studies for establishing the polymer design, which can report the change of the screw sense of the polymer backbone as fluorescence changes, are currently being undertaken in this laboratory.

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#### Notes and references

- R. P. Cheng, S. H. Gellman and W. F. DeGrado, *Chem Rev*, 2001, 101, 3219-3232.
- 50 2. J. J. L. M. Cornelissen, A. E. Rowan, R. J. M. Nolte and N. A. J. M. Sommerdijk, *Chem Rev*, 2001, **101**, 4039-4070.
  - D. J. Hill, M. J. Mio, R. B. Prince, T. S. Hughes and J. S. Moore, *Chem Rev*, 2001, **101**, 3893-4011.
- 4. T. Nakano and Y. Okamoto, Chem Rev, 2001, 101, 4013-4038.
- 55 5. E. Yashima, K. Maeda and T. Nishimura, *Chemistry A European Journal*, 2004, **10**, 42-51.
  - E. Yashima, K. Maeda, H. Iida, Y. Furusho and K. Nagai, *Chem Rev*, 2009, **109**, 6102-6211.
- T. Yamada, Y. Nagata and M. Suginome, *Chem Commun*, 2010, 46, 4914-4916.
  - T. Yamamoto and M. Suginome, Angew. Chem. Int. Ed., 2009, 48, 539-542.
  - T. Yamamoto, T. Yamada, Y. Nagata and M. Suginome, *J Am Chem Soc*, 2010, **132**, 7899-7901.
- 65 10. T. Yamamoto, Y. Akai, Y. Nagata and M. Suginome, *Angew. Chem. Int. Ed.*, 2011, **50**, 8844-8847.
  - 11. S. S. Lehrer, Method Enzymol, 1997, 278, 286-295.
  - G. Bains, A. B. Patel and V. Narayanaswami, *Molecules*, 2011, 16, 7909-7935.
- 70 13. A. Ueno, Supramol. Sci., 1996, 3, 31-36.
  - A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher and T. E. Rice, *Chem Rev*, 1997, 97, 1515-1566.
- 15. S. Karuppannan and J. C. Chambron, *Chem-Asian J*, 2011, **6**, 964-75 984.
  - 16. F. M. Winnik, Chem Rev, 1993, 93, 587-614.
  - 17. H. Zhao, F. Sanda and T. Masuda, Polymer, 2006, 47, 1584-1589.
  - 18. H. Z. Lin, K. Morino and E. Yashima, Chirality, 2008, 20, 386-392.
- B. Wardle, *Principles and applications of photochemistry*, Wiley,
   2009.
  - J. Lacour, D. Monchaud, G. Bernardinelli and F. Favarger, Org Lett, 2001, 3, 1407-1410.

