Eight-Membered-Ring-Forming Chain-Growth Cyclopolymerization of 2,2'-Diisocyano-1,1'-binaphthalenes for the Synthesis of Helical Poly([1,4]diazocine-2,3-diyl)s

Yukako Yoshinaga*, Ryo Nishimaru, Michinori Suginome*

Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan

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ABSTRACT: Novel helical macromolecules, poly([1,4]diazocine-2,3-diyl)s (PDACs), are synthesized by cyclopolymerization of 2,2'-diisocyano-1,1'-binaphthalenes in the presence of organonickel or organopalladium complexes as initiators, with the former being more efficient. The polymerization proceeds in a living fashion similar to the polymerization of monoisocyanides, but involves the formation of an eight-membered [1,4]diazocine ring, resulting in the exclusive formation of an array of [1,4]diazocine rings connected at their 2,3-positions without forming a monoiminomethylene unit. The structure of PDAC was identified by ^{13}C-labeling experiments and by the mass spectrum of the isolated living 2-([1,4]diazocinyl)palladium complex. The conformation of the main PDAC chain obtained from (*R*)-2,2'-diisocyano-1,1'-binaphthalene is deduced from DFT calculations, which reveal that the two C=N bonds in the diazocine ring form a dihedral angle of –73(±5)°, while the two inter-unit C=N bonds exhibit a nearly *anti* (+167(±4)°) orientation, resulting in the formation of a left-handed helical main chain. The enantiopure monomer polymerized significantly faster than the racemic monomer, forming stereoisomeric PDACs, the NMR spectra of which differ.

Cyclopolymerization, in which intramolecular cyclization of a bifunctional monomer precedes the propagation step, is recognized as a highly attractive polymerization pathway, since the cyclic structure of the repeating units is created during the polymerization.[1] A remarkable example was shown in the Zr-mediated cyclopolymerization of α,ω-dienes, which enabled the synthesis of optically active polymers containing a cyclopentane ring by using chiral initiators.[1d,e] The cyclopolymerization is not limited to alkene polymerization but has been largely restricted to easily formed cyclic structures, such as five- and six-membered rings, because it always competes with noncyclizing polymerization, in which the two reactive groups in a single monomer react without cyclization, eventually leading to cross-linking of two growing chains containing noncyclized units. Widening the scope of cyclopolymerization to monomer structures other than carbon–carbon multiple bonds as well as to larger ring systems is desired to expand the chemical space of macromolecular structures.

Isocyanide is a unique functional group with a structure that is isoelectric with carbon monoxide, leading to living polymerization in the presence of initiators to give polyisocyanides with helical conformation.[2] Monomers bearing two isocyano groups are expected to give cyclopolymerization products containing two C=N bonds in the formed ring (Figure 1(a)). However, the only example of the cyclopolymerization of such a monomer is diisocyanobenzene and its derivatives, which generate poly(quinoxaline-2,3-diyl)s (Figure 1(b)).[3] This polymerization has been utilized for the synthesis of a

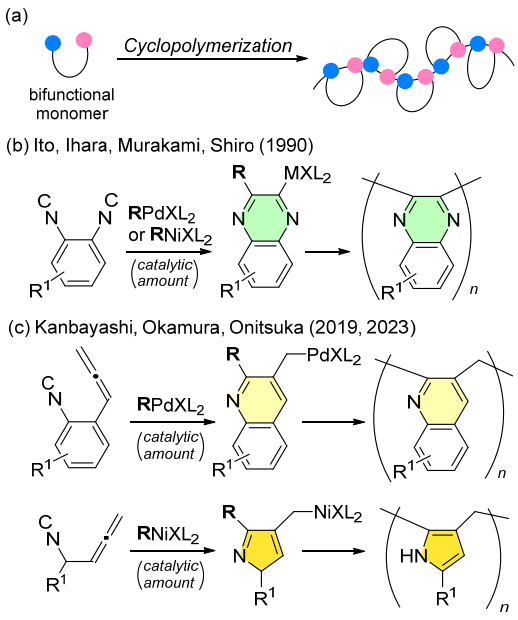


Figure 1. (a) Cyclopolymerization, (b) aromatizing cyclopolymerization of 1,2-diisocyanobenzene, and (c) aromatizing cyclopolymerization of allenyl-substituted isocyanide.

variety of chirality-switchable catalysts for asymmetric catalysis[4] and materials for circularly polarized light manipulation.[5] Utilization of isocyanides in cyclopolymerization has mostly been limited to 1,2-diisocyanobenzenes and the notable aromatizing cyclopolymerization of allenyl-substituted isocyanides.[6] The success of the cyclizing polymerization of 1,2-diisocyanobenzene was ascribed, in the initial reports, to energetically favorable aromatization.[3] We wondered whether cyclopolymerization of diisocyanides really relies upon aromatization.

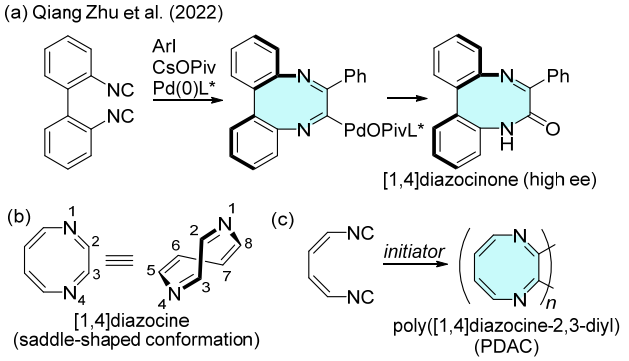


Figure 2. (a) Palladium-catalyzed reaction of 2,2'-diisocyanobiphenyl,[7] (b) the structure of [1,4]diazocine, and (c) possible cyclopolymerization pathway to poly([1,4]diazocine-2,3-diyl) derivatives.

The reaction of 2,2'-diisocyanobiphenyl with aryl iodides has been shown to afford aryl [1,4]diazocinone in the presence of palladium catalysts with stoichiometric metal carbonates (Figure 2(a)).[7] This report caught our eye because it was proposed that a [1,4]diazocinylpalladium intermediate is formed through successive insertion of two intramolecular isocyano groups. The [1,4]diazocine ring has attracted attention because of the unique nature of its rigid, twisted saddle-shaped conformation with a high inversion barrier (Figure 2(b)). Although reductive elimination of the C–O bond resulted in the formation of [1,4]diazocinones in the proposed mechanism, the palladium intermediate can be regarded as a direct living intermediate for cyclopolymerization (Figure 2(c)). To secure stereochemical simplicity in the produced polymer, we decided to use the corresponding binaphthyl derivatives of (*R*)-**1** in enantiopure form, bearing butyl groups to enhance the solubility of the resulting polymers.[8] Herein, we report the polymerization of 2,2'-diisocyano-1,1'-binaphthalene ((*R*)-**1**) in the presence of organonickel complexes as an initiator. Cyclopolymerization proceeded in a living mode to give poly([1,4]diazocine-2,3-diyl) (PDAC) derivatives featuring a left-handed helical structure. Notably, polymerization even proceeds with an organopalladium initiator, albeit with a slower polymerization rate.

(*R*)-6,6'-Dibutyl-2,2'-diisocyano-1,1'-binaphthalene ((*R*)-**1**), synthesized from (*R*)-1,1'-binaphthalene-2,2'-diol in seven steps (see the SI), was subjected to polymerization with a monomer/initiator ratio (M/I) of 40 in the presence of the arylnickel complex, *o*-TolNiCl(PMe$_3$)$_2$, which was found to be the best initiator in the polymerization of 1,2-diisocyanobenzenes (Figure 3(a); Table 1).[4,5,9] (*R*)-**1** was consumed completely after 2 h at room temperature to give **PDAC(40)** as a yellow solid that was soluble in solvent such as $CHCl_3$, THF, and toluene. By increasing the M/I to 100 and 300, the molecular weight (M_n) increased almost linearly to give higher polymers **PDAC(100)** and **PDAC(300)**, suggesting a chain-growth mechanism (Table 1, entries 1–3). This nature of the chain-growth polymerization was further confirmed by polymerization with sequential addition of monomer (Figure 3(b)). Thus, monomer **1** (20 equiv) was added in five portions at 2 h intervals, and the reaction mixture was analyzed by GPC after each step. The obtained GPC traces all remained unimodal with a monotonic increase of molecular weight, supporting the idea of a chain-growth mechanism.

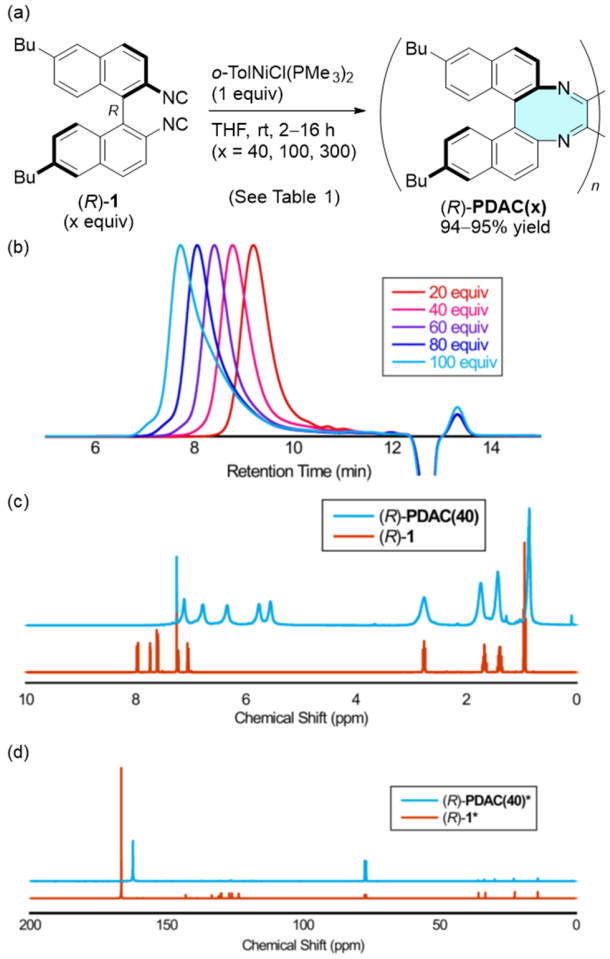
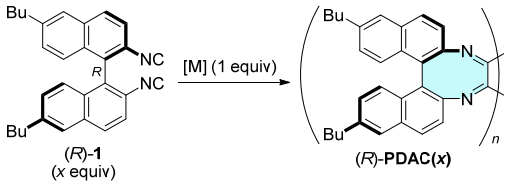


Figure 3. (a) Organonickel-initiated polymerization of (*R*)-**1**, (b) GPC traces of (*R*)-**PDAC** upon sequential monomer (20 equiv each) additions, (c) ^{1}H NMR of (*R*)-**1** and (*R*)-**PDAC(40)**, and (d) ^{13}C NMR of ^{13}C-labelled (*R*)-**1** and (*R*)-**PDAC(40)**.

The IR spectrum of isolated **PDAC(40)** contained no peak corresponding to the isocyano group (see the SI). The mass spectrum of **PDAC(40)** showed peaks with constant intervals corresponding to monomer molecular weight of 416 (see the SI). The ^{1}H NMR spectrum showed five broad signals in the aromatic region, suggesting the formation of a symmetrical unit structure (Scheme 1(c)). Polymerization of (*R*)-**1***, containing ^{13}C-labeled isocyano groups, gave **PDAC(40)***, which showed a single carbon signal at 162.26 ppm in the ^{13}C NMR spectrum (Scheme 1(d)). These results clearly suggest the formation of a

symmetrical ring structure through the cyclopolymerization process.

Table 1. Optimization of Polymerization of (*R*)-1 in the Presence of Nickel and Palladium Initiators



Entry	[M]	x	t (h)	Yield (%)	M_n (10^4)	M_w/M_n
1	^{o}TolNiCl(PMe$_3$)$_2$	40	2	95	1.34	1.41
2	^{o}TolNiCl(PMe$_3$)$_2$	100	2	95	3.42	1.94
3	^{o}TolNiCl(PMe$_3$)$_2$	300	16	94	7.38	3.05
4[b]	NiCl$_2$·6H$_2$O	40	76	(95)[a]	3.22	3.83
5[c]	NiCl$_2$(dppp)	40	76	(95)[a]	2.90	4.50
6[d]	NiCl$_2$(PPh$_3$)$_2$	40	76	(95)[a]	3.02	2.84
7	*o*TolPdI(PMe$_2$Ph)$_2$	40	96	(52)[a]	multimodal	
8[e]	*o*TolPdI(PMe$_2$Ph)$_2$	40	93	(95)[a]	1.09	1.35

[a] Yields based on GPC area ratio. [b] In THF/MeOH (95:5). [c] In THF/DCM (4:1). [d] In THF/MeOH (9:1). [e] At 50 °C.

The use of nickel(II) dichlorides with or without phosphine ligands led to the formation of **PDAC** with full conversion of the monomer, although its molecular weight distribution was significantly broader than that obtained with *o*-TolNiCl(PMe$_3$)$_2$ (Table 1, entries 4–6). Notably, the analogous organopalladium complex *o*-TolPdI(PMe$_2$Ph)$_2$ also catalyzed polymerization, although it required higher temperature (50 °C) and longer time (93 h) (entries 7 and 8).[10] It should be noted that the 1:1 reaction of (*R*)-**1** with *o*-TolPdI(PMe$_2$Ph)$_2$ gave [1,4]diazocinylpalladium complex (*R*)-**2**, which is formed through successive insertion of the two isocyano groups of (*R*)-**1** into the C–Pd bond and is considered to be a living intermediate (Figure 4(a)). Single-crystal X-ray analysis of (*R*)-**2** confirmed the formation of the [1,4]diazocine ring with its twisted, saddle-shaped structure (Figure 4(b)). Moreover, the crystal structure clearly suggests that the two σ-bonds at 2- and 3-positions of the diazocine ring, which take part in the formation of the polymer main chain, form a dihedral angle of –71° as a consequence of the negative dihedral angle of the (*R*)-configured 1,1'-binaphthyl moiety.

We are interested in the secondary structure of **PDAC**, the main chain of which is expected to have single-handed helical conformation through chirality transfer from the binaphthyl chirality. The measured circular dichroism (CD) spectra of (*R*)-**PDAC(40)** and (*S*)-**PDAC(40)**, which was obtained by polymerization of (*S*)-**1**, showed mirror image CD curves, which differ significantly from the CD curve of monomer **1** (Figure 5). **PDAC** with different polymerization degrees exhibited identical CD signals with no change of Δε on the basis of the concentration of monomer units. 2-Phenyl[1,4]diazocine derivative (*R*)-**DAC** was separately prepared as a model for comparison, and it exhibited a CD signal at a higher wavelength than that of (*R*)-**1**. These observations suggest that the signals at wavelengths higher than 320 nm arise from exciton coupling involving the imine C=N bonds.

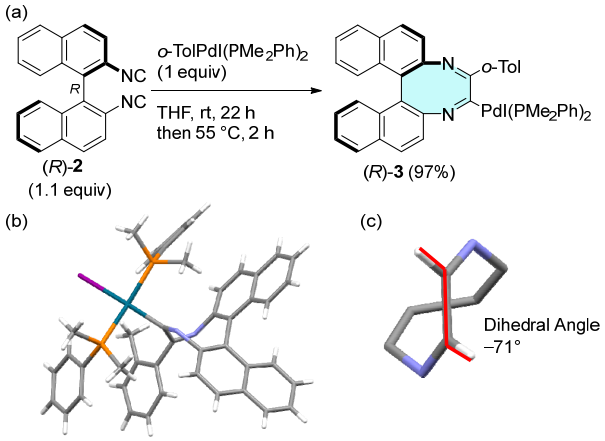


Figure 4. (a) Formation and (b) single-crystal X-ray structure of (*R*)-**2** (c) with its [1,4]diazocine core structure.

To gain more insight into the precise molecular conformation of **PDAC**, DFT calculation of a **PDAC** hexamer with no butyl groups were conducted. Geometry optimization and conformation search were initially performed on the basis of the unit structure obtained in the X-ray analysis of (*R*)-**3**, using CONFLEX software, MMFF94s force field within an energy window of 6.0 kcal/mol.[11] The obtained structure distribution suggests that one conformation has >99.9% contribution (see Supporting Information). The most probable conformation was further optimized by DFT calculations, giving a helical conformation (Figure 2(c)). In the optimized structure, the dihedral angles of the two C=N bonds in the ring and those in the neighboring ring are –73(±5)° and +167(±4)°, respectively. The whole structure of (*R*)-**PDAC** is therefore represented by a net left-handed helical structure, in which the intra-unit *M*-twist (–73°) is more predominant than the inter-unit *anti*-orientation (+167°).

The effect of the monomer chirality on polymerization and macromolecular properties was examined by the copolymerization of (*R*)-**1** and (*S*)-**1** with varied ratios. Polymerization of the racemate (0% ee) proceeded relatively slowly (22 h), giving CD-silent *rac*-**PDAC** in a good yield (entry 1, Figure 6(a,b)). The obtained polymer showed almost identical GPC trace and IR spectrum to those of (*R*)-**PDAC**, but its ^{1}H NMR spectrum exhibited much broader signals (Figure 6(c)). Interestingly, CD-silent *block-rac*-**PDAC** obtained by sequential addition of (*R*)- and (*S*)-**1** (20 equiv each) showed ^{1}H NMR spectra identical to that of (*R*)-**PDAC** (>99% ee) with sharper signals, suggesting that the formation of a stereoblock is not significant in the polymerization of the racemate. Polymerization of **1** with varied ee (20, 50, and 80% ee) all resulted in the formation of **PDAC** with different ^{1}H NMR spectra. Their CD spectra are shown in Figure 6(c), suggesting the enantiomeric ratio of monomer **1** has no impact on the CD signals, with the change of its intensities almost directly proportional to the ee of **1**. In particular, CD signals above 310 nm were found to be identical, with linear increases in their intensities with the increase of ee. These results suggest that the CD signals almost exclusively arise from each chiral monomer unit without involvement of inter-unit exciton couplings above 310 nm.

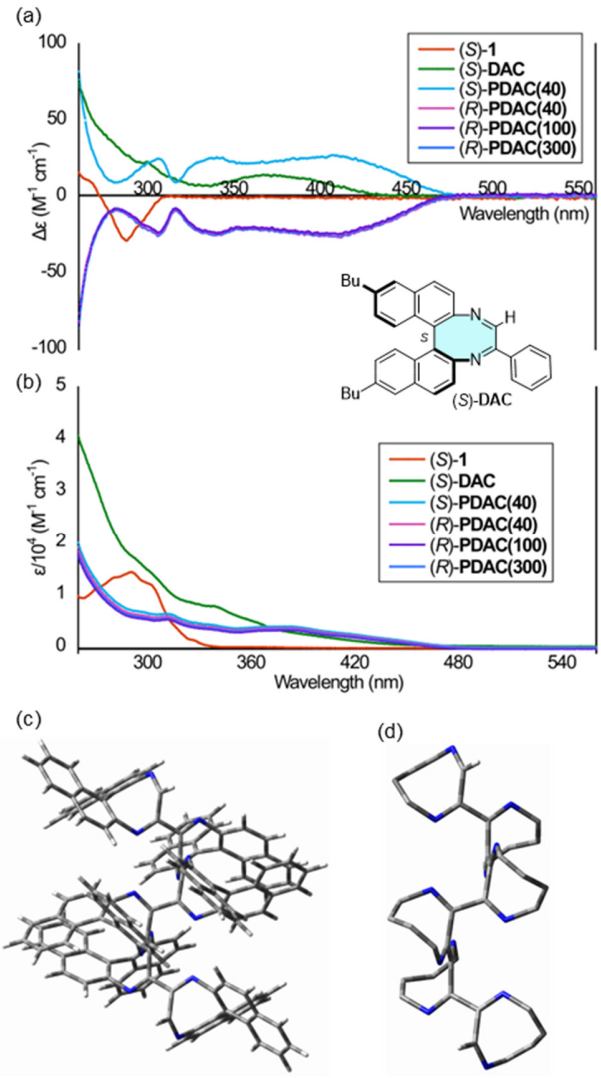
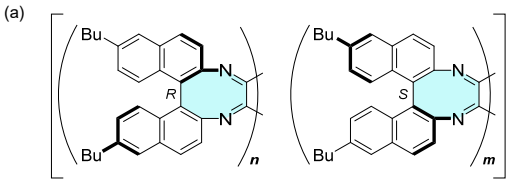


Figure 5. (a) CD and (b) UV-vis spectra of (*R*)-**1**, (*R*)-**3**, (*R*)-**PDAC(40, 100, 300)**, and (*S*)-**PDAC(40)**. (c) DFT-optimized structure of a (*R*)-**PDAC** hexamer and (d) its skeletal representation with the omission of the fused naphtho groups.

In conclusion, we have established that eight-membered-ring-forming cyclopolymerization of 2,2'-diisocyano-1,1'-binaphthalene through the use of organonickel or palladium complexes as initiators proceeds via a chain-growth mechanism. Moreover, the produced polymer **PDAC** is structurally novel with an array of rigid, saddle-shaped eight-membered rings. From the single-crystal X-ray analysis of monomeric living intermediate and DFT calculations of the corresponding hexamer, a left-handed helical structure is proposed. The CD signals mainly arise from the chiral structure of each monomer unit with no strong influence of inter-unit exciton coupling. This finding expands the scope of cyclopolymerization of diisocyanides, with which only aromatizing six-membered ring formation has been known, leading to the development of structurally new polymers including chiral helical polymers for new chiral molecular functions.



Entry	Copolymer	ee of **1**	Time (h)	Yield (%)	M_n (10^4)	M_w/M_n
1	poly((*R*)-**1**-*ran*-(*S*)-**1**)	0	22	88	1.15	1.76
2		20	(22) [a]	86	1.13	1.68
3		50	(22) [a]	92	1.18	1.64
4		80	(22) [a]	87	1.18	1.64
5 [b]		>99	2	95	1.34	1.41
6	poly((*R*)-**1**-*block*-(*S*)-**1**)	0	1+2	78	1.44	1.80

[a] unoptimized. [b] The same data as that shown in entry 1, Table 1.

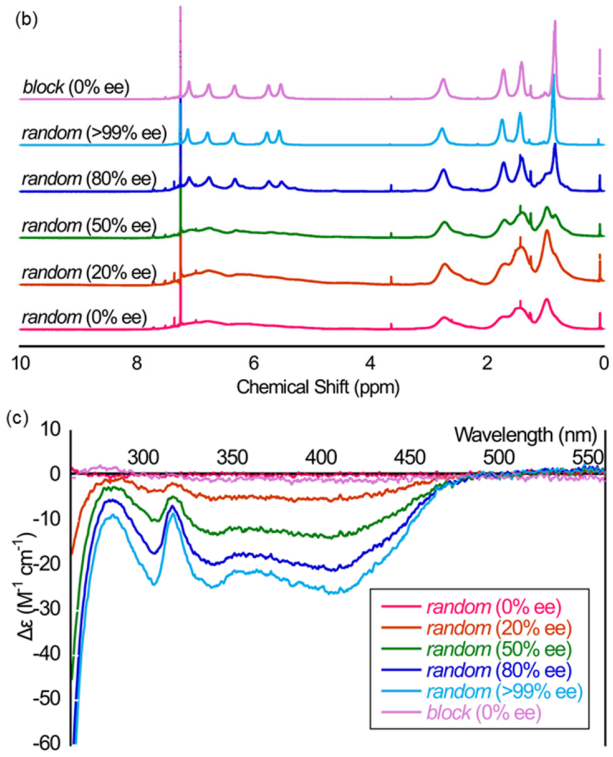


Figure 6. PDAC synthesized from **1** with varied enantiopurity. (a) Polymerization results of **PDAC** random or block copolymer, with varied enantiopurity, (b) ^{1}H NMR spectra ($CDCl_3$, 20 °C), and (c) CD spectra (Δε calculated based on conc. of monomer unit; methylcyclohexane, 20 °C).

ASSOCIATED CONTENT

Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

Accession Codes. CCDC 2384050 contain the supporting crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing-data_request@ccdc.cam.ac.uk, or by contacting The

CambridgeCrystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

Yukako Yoshinaga − Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan; orcid.org/0009-0002-1947-6554; Email: yoshinaga@sbchem.kyoto-u.ac.jp
Michinori Suginome − Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan; orcid.org/0000-0003-3023-2219; Email: suginome@sbchem.kyoto-u.ac.jp

Author Contributions

Y.Y. and M.S. designed and directed the project. R.N. and Y.Y. performed the experiments and analyzed the data. Y.Y. and M.S. co-wrote the paper. All authors have given approval for the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

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