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Fluorescent Poly(boron enaminoketonate): Synthesis via Direct Modification of Polyisoxazole Obtained by Click Polymerization of Homoditopic Nitrile *N*-Oxide and Diyne

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RUNNING HEAD: Fluorescent Poly(boron enaminoketonate)

ABSTRACT: Fluorescent poly(boron enaminoketonate)s (**PBEK**s) were synthesized via polycycloaddition of homoditopic nitrile *N*-oxide to diynes and subsequent polymer reactions. Click polycycloaddition of the nitrile *N*-oxide to various diynes effectively produced polyisoxazoles in high yields. Transformation of the polyisoxazoles afforded the corresponding fluorescent **PBEK**s via intermediary formation of poly(β-aminoenone) followed by the reaction with $(C_6F_5)_2BF\cdot OEt_2$. The optical properties of **PBEK**s were evaluated by the UV–vis and fluorescent spectra obtained under solution and solid states.

KEY WORDS Click Polymerization / Poly(boron enaminoketonate) / Homoditopic Nitrile *N*-Oxide / Fluorescence / Polyisoxazole

Introduction

Boron diketonate is a member of the boron-chelating dyes, and as a fluorophore, it has attracted much attention.[1-4] The optical properties of boron diketonate such as its large Stokes shift and two-photon absorption cross sections and the versatile applications based on the incorporation to various organic backbones provide its potential usefulness for a molecular probe,[5] laser,[6] and optical sensing applications.[7,8] Research by Fraser *et al.* on the applications to polymeric materials has reported synthesis of boron diketonate-containing polylactide and the oxygen-sensing property.[9] Moreover, Chujo *et al.* have demonstrated synthesis and emission color-tunings of the main chain-type poly(boron diketonate)s.[10-12] However, the synthetic difficulty of the boron diketonate-containing polymers restricts applicability of the polymer. Therefore, the use of boron enaminoketonate (BEK) as a substitute of boron diketonate is intriguing, because it is expected from the structural analogy that the BEK would serve as a fluorophore with good optical properties similar to those of boron diketonate.[13,14] Recently, Chujo *et al.* have revealed the optical properties of BEKs such as large Stokes shift and high-molar absorption coefficient that are quite similar to those of boron diketonates.[15]

On the other hand, we have reported a unique fluorescence control system of a BEK placed at the end of rotaxane axle.[16] The rotaxane-based BEK was readily prepared via sequential transformation of an isoxazole-containing rotaxane synthesized via a stable nitrile *N*-oxide-based click end capping reaction. The BEK exhibited a red-shift of the fluorescence maximum along with a remarkable enhancement of the fluorescence quantum yield through wheel translation to the fluorophore. In addition, we have also developed a synthetic method of producing poly(β-aminoenone) via a catalyst-free click polycycloaddition of a homoditopic nitrile *N*-oxide to diynes and selective reduction of N–O bonds.[17] Therefore, synthesis of poly(boron enaminoketonate) (**PBEK**) could be achieved by reacting the poly(β-aminoenone) with organoboron complex at the similar manner to the synthetic protocol of the rotaxane-based BEK. Herein, we describe the practical synthesis and properties of **PBEK** as a new fluorescent polymer. We emphasize upon the straightforward introduction capability of boron enaminoketonate skeletons into a polymer main chain on the basis of catalyst-free click polymerization of homoditopic stable nitrile *N*-oxide (Figure 1).

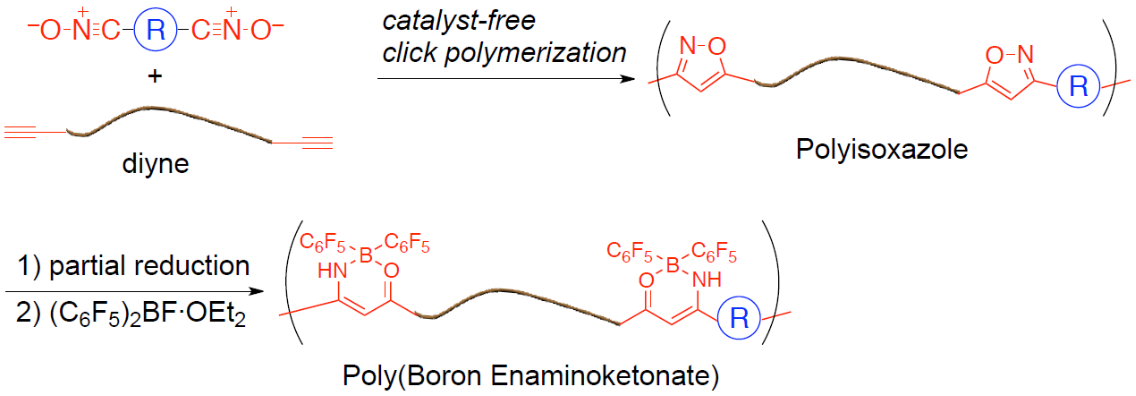


Figure 1 Click polymerization utilizing a homoditopic nitrile *N*-oxide with a diyne, and the transformation of a polyisoxazole into fluorescent **PBEK**.

Experimental Procedure

Materials: Dichloromethane was dried over freshly activated molecular sieves 4 A (MS 4A). Nitrile *N*-oxide **C** was prepared according to the literature.[18] All compounds given below bear the same formula numbers as used in the main text. Compounds unlabeled in the main text are labeled with letters [**A**–**K**].

Measurements: ^{1}H (400 MHz), ^{13}C (100 MHz), and ^{19}F NMR (400 MHz) NMR spectra were recorded on a JEOL AL-400 spectrometer using $CDCl_3$ and DMSO-d_6 as the solvents. ^{1}H- and ^{13}C NMR spectra were calibrated using residual undeuterated solvent or tetramethylsilane as the internal standard. ^{19}F NMR spectra were calibrated using $CFCl_3$ or fluorobenzene as the internal standards. IR spectra were recorded on a JASCO FT/IR-230 spectrometer. Melting points were measured on a MELTING POINT APPARATUS SMP3 (Stuart Scientific) instrument. MALDI–TOF MS spectra were measured with a Shimadzu AXIMA-CFR mass spectrometer using a dithranol matrix. High-resolution mass spectra (FAB-HRMS) were taken by an ICP-MS (Seiko Instruments, SPQ-9000) at the Center for Advanced Materials Analysis, Tokyo Institute of Technology on request. UV-vis spectra of **PBEK**s in a solution state were taken by a JASCO V-550 spectrophotometer. Fluorescence emission spectra of **PBEK**s in a solution state were taken by JASCO FP-6500 spectrofluorometer and the quantum yields were calculated on the basis of the fluorescent intensity of 9,10-diphenylanthracene as a reference standard. To evaluate the UV-vis and the emission spectra of **PBEK**s in a solid state, the polymer (**poly-3** and **PEG-3)** was dispersed in an Ar-saturated cyclohexane solution 2.5 mL (0.3 mg•mL^{-1}) by reprecipitation of a solution of the polymer in CH_2Cl_2 (0.2 mL), and then the emission spectra and the quantum yields were measured by a calibrated integrating sphere and a multi-channel spectrometer (C9920-02G: Hamamatsu Photonics) with 388 nm light for excitation. The emission quantum yields were obtained by using the emission intensities at 400–800 nm regions.

Synthesis of model compounds for the evaluation of the optical properties.

Synthesis of 1-methoxy-4-trimethylsilylethynylbenzene **A**[19]

To a suspension of 1-iodo-4-methoxybenzene (4.58 g, 24.5 mmol), $Pd(PPh_3)_3$ (844 mg, 0.73 mmol), and CuI (140 mg, 0.73 mmol) in Et_3N (80 mL) was added trimethylsilyl acetylene (5.00 mL, 36.1 mmol) at room temperature. The mixture was warmed to 80 °C, stirred for 3 h argon atmosphere, filtrated, and concentrated in vacuo. The crude was purified by silica gel column chromatography (hexane:ethyl acetate = 9:1) to give **A (**5.85 g, 28.6 mmol, quant.) as a brown oil; ^1H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.40 (d, $J = 9.0$ Hz, 2H), 6.81 (d, $J = 9.0$ Hz, 2H), 3.81 (s, 3H), 0.24 (s, 9H) ppm.

Synthesis of 1-methoxy-4-ethynylbenzene **B**

To a solution of **A** (5.85 g, 24.5 mmol) in MeOH (100 mL) was added K_2CO_3 (6.77 g, 49.0 mmol) at room temperature. The mixture was warmed to 40 ºC, stirred for 3 h under argon atmosphere, and concentrated in vacuo. Sat. aq. $NaHCO_3$ (150 mL) was added to the mixture and the products were extracted with EtOAc. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude was purified by short flash column chromathography on silica gel (hexane:EtOAc = 9:1) to yield **B** (3.07 g, 23.2 mmol, 95%) as a brown oil. The crude was used for next reaction without further purification; IR (NaCl) υ 3287, 3004, 2959, 2837, 2540, 2106, 1893, 1606, 1571, 1505, 1464, 1442, 1291, 1249, 1171, 1108, 1031, 833, 641, 606, 537 cm^{-1}; ^1H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.43 (d, *J* = 8.9 Hz, 2H), 6.84 (d, *J* = 8.9 Hz, 2H), 3.81 (s. 3H), 3.00 (s, 1H) ppm; ^{13}C NMR (100 MHz, 298 K, $CDCl_3$): δ 160.1, 133.8, 114.3, 114.1, 83.9, 76.2, 55.3 ppm.

Synthesis of pentafluorophenyl magnesium bromide[20]

To a mixture of magnesium (392 mg, 16.1 mmol) in Et_2O (30 mL) was added bromopentafluorobenzene (2.10 mL, 16.6 mL) dropwise under argon atmosphere at room temperature and the mixture was refluxed for 3 h to give pentafluorophenyl magnesium bromide. This crude was used for the next reaction without purification.

Synthesis of $(C_6F_5)_2BF \cdot OEt_2$ **5**[20]

The freshly prepared C_6F_5MgBr solution in Et_2O (30 mL) solution was added to a solution of $BF_3 \cdot OEt_2$ (1.02 mL, 8.04 mmol) in Et_2O (20 mL) at 0 °C at once. After stirring for 30 min, the solvent was evaporated at 0 °C to give **5** as a gray solid. This crude solid was used for the next reaction without purification.

Synthesis of isoxazole **D**

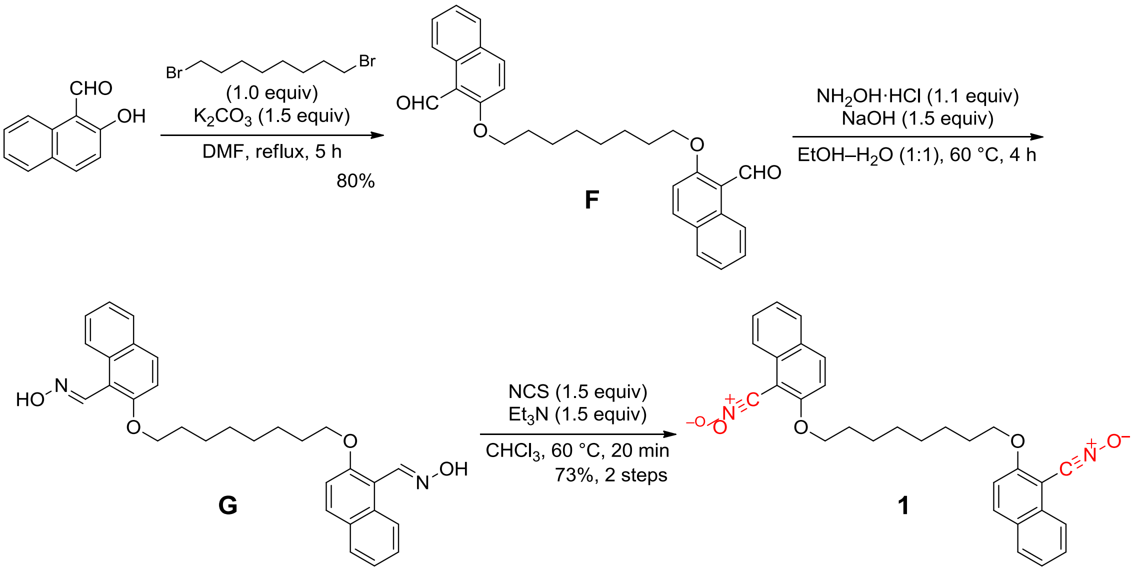
To a solution of 4-ethynylanisole (498 mg, 3.77 mmol) in $CHCl_3$ (10 mL) was added nitrile *N*-oxide **C** (500 mg, 2.51 mmol). The solution was refluxed for 5 h. The crude was purified by short flash column chromathography on silica gel (hexane, then $CHCl_3$) to yield **D** (588 mg, 1.77 mmol, 71%) as light brown solids; m.p. 96.9–97.9 ºC; IR (KBr) υ 2935, 2835, 1613, 1512, 1433, 1353, 1304, 1254, 1176, 1078, 1026, 835, 804, 752, 655 cm^{-1}; ^{1}H NMR (400 MHz, 298 K, CDCl$_3$) δ 7.97 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 8.6 Hz, 1H), 7.83 (d, *J* = 9.0 Hz, 1H), 7.83 (d, *J* = 9.0 Hz, 2H), 7.45 (dd, *J* = 8.2, 6.8 Hz, 1H), 7.38 (dd, *J* = 8.6, 6.8 Hz, 1H), 7.37 (d, *J* = 9.0 Hz, 1H), 7.02 (d, *J* = 9.0 Hz, 2H), 6.61 (s, 1H), 3.94 (s, 3H), 3.89 (s, 3H) ppm; MALDI–TOF MS (matrix: dithranol) Calc'd for $C_{21}H_{17}NO_3$ $[M+Na]^+$ 354.11, found: 354.09.

Synthesis of enaminoketone **E**

To a solution of isoxazole **D** (200 mg, 0.604 mmol) in CH_3CN (5 mL) and water (1.2 mL) was added $Mo(CO)_6$ (191 mg, 0.725 mmol). The mixture was refluxed for 10 h, and evaporated in vacuo. The crude was purified by short flash column chromathography on silica gel (hexane:EtOAc = 2:1) to yield **E** (174 mg, 0.522 mmol, 86%) as brown solids. The crude was used for next reaction without further purification; IR (KBr) υ 3449, 2935, 2838, 1595, 1503, 1378, 1252, 1174, 1076, 1028 cm^{-1}; ^{1}H NMR (400 MHz, 298 K, CDCl$_3$) δ 10.50 (br, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 9.0 Hz, 2H), 7.82 (d, *J* = 8.7 Hz, 1H), 7.47 (dd, *J* = 8.5, 6.9 Hz, 1H), 7.38 (dd, *J* = 8.5, 6.9 Hz, 1H), 7.34 (d, *J* = 8.7 Hz, 1H), 6.89 (d, *J* = 9.0 Hz, 2H), 5.92 (s, 1H), 5.32 (br, 1H), 3.97 (s, 3H), 3.84 (s, 3H) ppm.

Synthesis of **6**

$(C_6H_5)_2BF\cdot OEt_2$ **5** (70.5 mg, 0.161 mmol) was added to a solution of **E** (10.3 mg, 33.1 μmol) in CH_2Cl_2 (0.5 mL) under argon atmosphere. The reaction mixture was stirred at room temperature for 2 h, and concentrated in vacuo. The crude was purified by short flash column chromathography on silica gel (CHCl3) and then HPLC to yield **6** (22.3 mg, 32.9 μmol, 99%) as yellow solids; m.p. 83.2–84.6 ºC; IR (KBr) υ 3422, 2937, 2844, 1654, 1607, 1508, 1477, 1377, 1261, 1178, 1090, 979, 811, 797, 752 cm^{-1}; ^1H NMR (400 MHz, 298 K, $CDCl_3$) δ 8.01 (d, *J* = 8.6 Hz, 2H), 8.00 (d, *J* = 9.3 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.81 (br, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.48 (dd, *J* = 8.4, 7.0 Hz, 1H), 7.42 (dd, *J* = 8.0, 7.0 Hz, 1H), 7.34 (d, *J* = 9.3 Hz, 1H), 6.97 (d, *J* = 8.6 Hz, 2H), 6.15 (s, 1H), 3.89 (s, 3H), 3.88 (s, 3H) ppm; ^{13}C NMR (100 MHz, 298 K, $CDCl_3$) δ 173.7, 168.5, 164.0, 154.6, 133.3, 131.4, 130.7, 129.0, 128.9, 128.5, 126.0, 124.9, 123.8, 118.2, 114.5, 113.0, 96.0, 56.6, 55.9 ppm; ^{19}F NMR (400 MHz, 298 K, $CDCl_3$) δ –137.25 (s, 2F), –157.99 (s, 1F), –164.19 (s, 2F) ppm; MALDI–TOF MS (matrix: dithranol) Calc’d for $C_{33}H_{18}BF_{10}NO_3$ $[M+H]^+$ 678.13, found: 678.14.



Scheme 1 Synthesis of homoditopic nitrile *N*-oxide **1**.

Synthesis of bisaldehyde **F**

To a solution of 2-hydroxy-1-naphthaldehyde (12.7 g, 73.8 mmol) and 1,8-dibromooctane (6.76 mL, 36.8 mmol) in DMF (40 mL) was added K_2CO_3 (15.2 g, 110 mmol) at room temperature. The mixture was refluxed for 5 h. The mixture was cooled to room temperature, quenched by the addition of excess amount of water, and filtered. The crude was recrystallized in $CHCl_3$ and the resulting precipitates were washed with acetone to yield ditopic aldehyde **F** (13.4 g, 29.4 mmol, 80%) as pale pink solids; m.p. 161.3–165.2 ºC; IR (KBr) υ 2923, 2858, 1666, 1587, 1512, 1437, 1343, 1249, 1154, 1058, 814, 769 cm^{-1}; ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 10.93 (s, 2H), 9.28 (d, *J* = 8.8 Hz, 2H), 8.04 (d, *J* = 9.2 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.63–7.60 (m, 2H), 7.43–7.39 (m, 2H), 7.28 (d, *J* = 9.2 Hz, 2H), 4.23 (t, *J* = 6.6 Hz, 4H), 1.90 (tt, *J* = 6.6, 6.6 Hz, 4H), 1.57–1.51 (m, 4H), 1.45–1.41 (m, 4H) ppm; ^{13}C NMR (100 MHz, 298 K, $CDCl_3$) δ 192.3, 163.9, 137.7, 131.7, 130.0, 128.6, 128.4, 125.1, 124.8, 116.9, 113.7, 69.6, 29.4, 29.4, 26.2 ppm; FAB HR-MS (matrix: NBA) Calc'd for $C_{30}H_{31}NaO_4$ $[M+H]^+$ 455.2222, found: 455.2232.

Synthesis of bisoxime **G**

To a mixture of ditopic aldehyde **F** (18.5 g, 40.7 mmol) in EtOH (150 mL) was added a solution of $NH_2OH·HCl$ (6.22 g, 89.5 mmol) and NaOH (4.88 g, 120 mmol) in water (150 mL) at 0 ºC. The mixture was warmed to 60 ºC and stirred for 4 h. The solution was cooled to room temperature and quenched by the addition of excess amount of water. The resulting precipitates were filtered and washed with water, methanol, and hot $CHCl_3$ to yield ditopic oxime **G** (0.800 g, 43.0 mmol, quant.) as white solids. The crude was used for next reaction without further purification; m.p. 159.6–164.5 ºC; IR (KBr) υ 3297, 2941, 2857, 1632, 1593, 1513, 1463, 1440, 1318, 1247, 1181, 1063, 955, 914, 803, 751, 687, 641 cm^{-1}; ^{1}H NMR (400 MHz, 298 K, DMSO-d$_6$) δ 11.31 (s, 2H), 8.86 (d, *J* = 8.5 Hz, 2H), 8.68 (s, 2H), 7.96 (d, *J* = 9.0 Hz, 2H), 7.88 (d, *J* = 8.1 Hz, 2H), 7.54–7.50 (m, 2H), 7.46 (d, *J* = 9.0 Hz, 2H), 7.41–7.37 (m, 2H), 4.17 (t, *J* = 6.1 Hz, 4H), 1.78 (tt, *J* = 6.1, 6.1 Hz, 4H) 1.49–1.37 (m, 8H) ppm; ^{13}C NMR (100 MHz, 298 K, CDCl$_3$) δ 155.9, 154.4, 131.6, 130.8, 128.7, 128.4, 127.5, 125.6, 123.8, 114.6, 113.4, 69.0, 28.8, 28.7, 25.5 ppm; FAB HR-MS (matrix: NBA) Calc'd for $C_{30}H_{33}N_2O_4$ [M+H]$^+$ 485.2440, found: 485.2437.

Synthesis of **1**

To a mixture of ditopic oxime **G** (1.00 g, 2.06 mmol) in CHCl$_3$ (400 mL) was added Et$_3$N (861 μL, 6.18 mmol) and *N*-chlorosuccinimide (825 mg, 6.18 mmol) at 0 ºC. The mixture was warmed to 60 ºC and stirred for 20 min. The mixture was cooled to room temperature and quenched by the addition of water. The organic layer was dried over MgSO$_4$, filtered, and concentrated in vacuo. The crude was purified by short flash column chromathography on silica gel ($CHCl_3$) to yield the ditopic nitrile *N*-oxide **1** (716 mg, 1.49 mmol, 73%) as pale yellow solids; m.p. 119.5–120.7 ºC; IR (KBr) υ 2940, 2857, 2295, 1622, 1589, 1510, 1463, 1436, 1402, 1339, 1312, 1275, 1245, 1156, 1065, 1016, 995, 909, 806, 756, 669, 532 cm^{-1}; ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.95 (d, J = 8.6 Hz, 2H), 7.92 (d, J = 8.9 Hz, 2H), 7.81 (d, J = 8.3 Hz, 2H), 7.57 (dd, J = 8.6, 7.1 Hz, 2H), 7.41 (dd, J = 8.9, 7.1 Hz, 2H), 7.25 (d, J = 8.3 Hz, 2H), 4.22 (t, J = 6.4 Hz, 4H), 1.90 (tt, J = 6.4, 6.4 Hz, 4H), 1.59-1.47 (m, 8H) ppm; ^{13}C NMR (100 MHz, 298 K, $CDCl_3$) δ 161.3, 134.5, 133.1, 128.9, 128.8, 128.6, 125.1, 124.1, 113.5, 96.7, 69.9, 34.9, 29.4, 29.3, 26.0 ppm; FAB HR-MS (matrix: NBA) Calc'd for $C_{30}H_{28}N_2O_4Na$ $[M+Na]^+$ 503.1947, found: 503.1962.

Synthesis of 1-hydroxy-4-trimethylsilylethynylbenzene **H**[21,22]

To a suspension of *p*-iodophenol (5.30 g, 24.5 mmol), $Pd(PPh_3)_3$ (844 mg, 0.73 mmol) and CuI (140 mg, 0.73 mmol) in Et_3N (80 mL) was added trimethylsilyl acetylene (5.00 mL, 36.1 mmol). The solution was stirred for 3 h at 80 °C under argon atmosphere, filtrated and evaporated. The crude was purified by silica gel column chromatography (hexane:ethyl acetate = 9:1, then 1:1) to yield **H** a black oil (4.07 g, 21.4 mmol, 87%); ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.36 (d, *J* = 8.3 Hz, 2H), 6.75 (d, *J* = 8.3 Hz, 2H), 0.23 (s, 9H) ppm; ^{13}C NMR (100 MHz, 298 K, $CDCl_3$): δ 156.3, 134.0, 115.8, 115.4, 105.8, 92.9, 0.34 ppm.

Synthesis of 1-ethynyl-4-hydroxybenzene **I**[23]

To a solution of **H** (3.22 g, 16.9 mmol) in MeOH (100 mL) was added K_2CO_3 (4.56 g, 33 mmol). The mixture was stirred for 3 h at 40 ºC under argon atmosphere, and concentrated in vacuo. Sat. aq. $NaHCO_3$ (40 mL) was added to the mixture and the products were extracted with EtOAc. The combined organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The crude was purified by short flash column chromathography on silica gel (hexane:EtOAc = 9:1) to yield **I** (0.649 g, 5.49 mmol, 32%) as a black oil. The crude was used for next reaction without further purification; ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.39 (d, *J* = 8.5 Hz, 2H), 6.78 (d, *J* = 8.5 Hz, 2H), 5.17 (br, 1H), 2.99 (s, 1H) ppm.

Synthesis of **2** using **H**

To a solution of **H** (3.27 g, 17.2 mmol) and 1,8-dibromooctane (1.40 g, 5.74 mmol) in DMF (50 mL) was added K_2CO_3 (2.38 g, 17.2 mmol) at room temperature. The mixture was stirred at 100 ºC for 5 h, filtered and the solution was purified by short flash column chromathography on silica gel (hexane:$CHCl_3$ = 2:1). To the solution of the solid in THF (10 mL) was added TBAF 1mol/mL THF solution (0.5 mL). The solution was stirred for 1 h, washed by sat. aq. NH_4Cl, water and brine, and the organic layer was dried over $MgSO_4$ and concentrated in vacuo. The crude was purified by short flash column chromathography on silica gel (hexane:$CHCl_3$ = 2:1, then 1:1) and HPLC to yield **2** (192 mg, 0.554 mmol, 10%) as white solids; IR (KBr) υ 3299, 2940, 2105, 1606, 1509, 1467, 1291, 1253, 1171, 1032, 837, 610 cm^{-1}; ^1H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.41 (d, *J* = 8.3 Hz, 2H), 6.83 (d, *J* = 8.3 Hz, 2H), 3.95 (t, *J* = 6.5 Hz, 2H), 2.99 (s, 1H), 1.78 (tt, *J* = 6.5, 6.5 Hz, 2H), 1.52-1.38 (m, 4H) ppm; ^{13}C NMR (100 MHz, 298 K, $CDCl_3$) δ 159.6, 133.7, 114.5, 114.0, 83.9, 75.8, 68.1, 29.4, 29.2, 26.0 ppm.

Synthesis of **2** using **I**

To a solution of **I** (300 mg, 2.54 mmol) and 1,8-dibromooctane (0.200 mL, 1.21 mmol) in DMF (5.0 mL) was added K_2CO_3 (502 mg, 3.63 mmol) at room temperature. The mixture was stirred at 100 ºC for 5 h. The mixture was cooled to room temperature, diluted with Et_2O, washed with water and brine, and dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude was purified by short flash column chromathography on silica gel (hexane:$CHCl_3$ = 2:1) to yield **2** (112 mg, 0.323 mmol, 27%) as white solids. The crude was used for next reaction without further purification; IR (KBr) υ 3299, 2940, 2105, 1606, 1509, 1467, 1291, 1253, 1171, 1032, 837, 610 cm^{-1}; ^1H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.41 (d, *J* = 8.3 Hz, 2H), 6.83 (d, *J* = 8.3 Hz, 2H), 3.95 (t, *J* = 6.5 Hz, 2H), 2.99 (s, 1H), 1.78 (tt, *J* = 6.5, 6.5 Hz, 2H), 1.52−1.38 (m, 4H) ppm; ^{13}C NMR (100 MHz, 298 K, $CDCl_3$) δ 159.6, 133.7, 114.5, 114.0, 83.9, 75.8, 68.1, 29.4, 29.2, 26.0 ppm.

Synthesis of bisTsO-PEG **J**

To a solution of PEG (M_n 2000, 12.2 g, 6.10 mmol) in CH_2Cl_2 (40 mL) was added tosyl chloride (13.2 g, 122 mmol), Et_3N (17.0 mL, 122 mmol) and DMAP (149 mg, 1.22

mmol) at 0 ºC. The solution was stirred for 3 h. To the solution was added excess amount of Et_2O and the mixture was cooled to 0 ºC. The resulting precipitates were filtered, then reprecipitated into cold EtOH. The resulting solids were collected by filtration to yield **J (**12.4 g, 5.39 mmol, 88%) as a white solid. The crude was used for next reaction without further purification; ^1H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.79 (d, J = 8.4 Hz), 7.34 (d, J = 8.4 Hz), 4.16 (t, J = 4.6 Hz), 3.72–3.60 (m, 4H), 2.45 (s) ppm; T_m 40 ºC; T_g –41 ºC; T_{d5} 235 ºC; T_{d10} 251 ºC.

Synthesis of **3**

To a solution of **H** (1.00 g, 3.64 mmol) and K_2CO_3 (305 mg, 2.21 mmol) in DMF (10 mL) was added **J** (2.00 g, 0.883 mmol, M_n = 2300) at room temperature. The solution was stirred at 80 ºC for 12 h. To the solution was added excess amount of water. The products were extracted with EtOAc, dried over $MgSO_4$, and concentrated in vacuo. The products were reprecipitated into cold MeOH, and it was dissolved in THF (10 mL), and TBAF 1 M in THF, 0.2 mL) was added. The solution was stirred for 1 h at room temperature. The crude was reprecipitated into cold MeOH, and purified by mixing activated charcoal at 50 ºC for 12 h to yield **3** (539 mg, 0.245 mmol, 28%) as a white solid; ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.41 (d, J = 8.4 Hz), 6.85 (d, J = 8.4 Hz), 4.13 (t, J = 4.6 Hz), 3.85 (t, J = 4.6 Hz), 3.76–3.56 (m, 4H), 3.00 (s) ppm; M_n = 3100, M_w = 3300, M_w/M_n = 1.04 (estimated by SEC based on PEG standards); T_m 46 ºC; T_g –34 ºC; T_{d5} 360 ºC; T_{d10} 377 ºC.

Synthesis of bisTsO-PTHF **K**

To a solution of PolyTHF (M_n 2900, 14.5 g, 5.00 mmol) in CH_2Cl_2 (30 mL) was added TsCl (9.53 g, 50.0 mmol), Et_3N (6.97 mL, 50.0 mmol) and DMAP (61.1 mg, 0.500 mmol) at 0 ºC, and the solution was stirred for 3 h. The crude was precipitated into cold MeOH. The resulting solids were filtered to yield **K** (11.7 g, 3.66 mmol, 73%) as white solids. The crude was used for next reaction without further purification; ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.78 (d, J = 8.2 Hz), 7.34 (d, J = 8.2 Hz), 4.05 (t, J = 6.4 Hz), 3.58–3.33 (m, 4H), 2.45 (s), 1.75–1.39 (m, 4H) ppm; T_{d5} 190 ºC; T_{d10} 202 ºC.

Synthesis of **4**

To a solution of **H** (1.28 g, 4.68 mmol) and K_2CO_3 (305 mg, 2.21 mmol) in DMF (10 mL) was added **O** (5.00 g, M_n = 3200, 1.56 mmol) at room temperature. The solution was stirred at 100 ºC for 6 h. The precipitates from cold MeOH was dissolved in THF (10 mL), and TBAF 1mol/mL THF solution (0.2 mL) was added. The solution was stirred for 1 h. The crude was reprecipitated from cold MeOH and purified by mixing activated charcoal at 50 ºC for 12 h to yield **4** (3.13 g, 1.01 mmol, 65%) as white solids. The crude was used for next reaction without further purification; ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.41 (d, J = 8.8 Hz), 6.82 (d, J = 8.8 Hz), 3.98 (t, J = 6.1 Hz), 3.48–3.35 (m, 4H), 2.99 (s, 2H), 1.89–1.50 (m, 4H) ppm; M_n 3200; M_w 4200; M_w/M_n 1.34 (estimated by SEC based on PEG standards); T_m 32 ºC; T_g –71 ºC; T_{d5} 334 ºC; T_{d10} 349 ºC.

Typical procedure for the polycycloaddition of homoditopic nitrile *N*-oxide **1** with dialkyne: Synthesis of polyisoxazole **poly-1**

The solution of **1** (210 mg, 0.436 mmol) and 1,8-bis(4-ethynylphenoxy)octane (151 mg, 0.436 mmol) in $CHCl_3$ (300 μL) was refluxed for 20 h. The crude was reprecipitated into MeOH to give a solid, which was filtered and dried in vacuo at room temperature for 12 h to yield **poly-1** (362 mg, 0.438 mmol, quant.) as a brown solid; IR (KBr) υ 3437, 2931, 1615, 1512, 1250, 1063, 807 cm^{-1}; ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.96 (d, J = 8.6 Hz, 2H), 7.89 (d, J = 9.1 Hz, 2H), 7.78 (d, J = 7.4 Hz, 2H), 7.73 (d, J = 8.7 Hz, 4H), 7.45–7.27 (m, 6H), 6.91 (d, J = 8.7 Hz, 4H), 6.57 (s, 2H), 4.04–3.98 (m, 4H), 3.93–3.49 (m, 4H), 1.76–1.66 (m, 4H), 1.63–1.58 (m, 4H), 1.43–1.11 (m, 12H) ppm; M_n 30000; M_w 51000; M_w/M_n 1.70 (estimated by SEC based on PS standards); M_n 12000; M_w 21000; M_w/M_n 1.81 (estimated by SEC based on PEG standards); T_m 90.3 ºC; T_{d5} 323 ºC; T_{d10} 336 ºC.

PEG-1: IR (KBr) υ 2875, 1619, 1512, 1463, 1351, 1252, 1108, 951, 843 cm^{-1}; ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.97–7.75 (m), 7.46–7.27 (m), 7.01–6.96 (m), 6.60 (s), 4.13–3.47 (m, 4H), 1.65–1.17 (m) ppm; M_n 16000; M_w 25000; M_w/M_n 1.60 (estimated by SEC based on PEG standards); T_m 38.9 ºC; T_{d5} 277 ºC; T_{d10} 316 ºC.

PTHF-1: IR (NaCl) υ 2939, 2855, 2795, 1616, 1509, 1446, 1367, 1248, 1113, 810, 749

cm^{-1}; ^{1}H NMR (400 MHz, 298K, $CDCl_3$) δ 7.98–7.91 (m), 7.83–7.74 (m), 7.49–7.29 (m), 6.95–6.93 (m), 6.60 (s), 4.21–3.22 (m, 4H), 1.89–1.17 (m, 4H) ppm; M_n 7500; M_w 12000; M_w/M_n 1.66 (estimated by SEC based on PEG standards); T_m 24.9 ºC; T_{d5} 269 ºC; T_{d10} 295 ºC.

Typical procedure for the reduction of polyisoxazole: Synthesis of polyenaminoketone **poly-2**

To a mixture of **poly-1** (250 mg, 0.302 mmol) in DMF (10 mL) and water (1.0 mL) was added $Mo(CO)_6$ (79.7 mg, 0.302 mmol). The mixture was heated at 90 ºC and stirred for 12 h. The crude mixture was reprecipitated into Et_2O to give a solid, which was dried in vacuo at room temperature for 12 h to yield **poly-2** (75.6 mg, 0.0910 mmol, 30%) as a brown solid; IR (KBr) υ 3458, 2931, 2855, 1595, 1503, 1464, 1380, 1503, 1464, 1380, 1247, 1170, 1072, 1020, 809, 785, 749 cm^{-1}; ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 10.47 (br, 2H), 8.00–7.68 (m, 10H), 7.46–7.07 (m, 6H), 6.83–6.72 (m, 4H), 5.87 (s, 2H), 5.42 (br, 2H), 4.07–3.97 (m, 4H), 3.94–3.81 (m, 4H), 1.77–1.55 (m, 8H), 1.42–1.11 (m, 16H) ppm; M_n 16000; M_w 24000; M_w/M_n 1.50 (estimated by SEC based on PS standards); M_n 5600; M_w 8700; M_w/M_n 1.56 (estimated by SEC based on PEG standards).

PEG-2: IR (KBr) υ 2880, 1964, 1731, 1597, 1530, 1505, 1468, 1348, 1251, 1111, 951, 844, 526 cm^{-1}; ^1H NMR (400 MHz, 298 K, $CDCl_3$) δ 10.49 (br), 8.02–7.79 (m), 7.47–7.27 (m), 6.85–6.82 (m), 5.88 (s), 5.58 (br), 4.09–3.46 (m, 4H), 1.75–1.21 (m) ppm; M_n 9700; M_w 27000; M_w/M_n 2.77 (estimated by SEC based on PEG standards).

PTHF-2: IR (NaCl) υ 2939, 2856, 2795, 1598, 1467, 1368, 1246, 1112, 955, 808, 750 cm^{-1}; ^1H NMR (400 MHz, 298 K, $CDCl_3$) δ 10.49 (br), 8.02–7.29 (m), 6.94–6.88 (m), 5.88 (s), 4.17–3.94 (m), 3.73–3.33 (m, 4H), 3.32–3.24 (m), 2.01–1.54 (m, 4H), 1.54–1.00 (m) ppm; M_n 7900; M_w 44000; M_w/M_n 5.55 (estimated by SEC based on PEG standards).

Typical procedure for the complexation of poly(enaminoketone) with $(C_6F_5)_2BF$ **5**: Synthesis of poly(boron enaminoketonate) **poly-3**

To a solution of poly(enaminoketone) **poly-2** (73.7 mg, 88.7 μmol) in anhydrous dichloromethane (1.5 mL) was added $(C_6F_5)_2BF \cdot OEt_2$ (389 mg, 887 μmol). The solution was stirred at room temperature for 2 h. The crude was reprecipitated into Et_2O to give a solid, which was dried in vacuo at room temperature for 12 h to yield **poly-3** (133 mg, 87.6 μmol, 99%) as a brown solid; IR (NaCl) υ 2930, 2855, 1646, 1607, 1558, 1506, 1475, 1374, 1259, 1206, 1177, 1091, 978, 807 cm^{-1}; ^1H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.97–7.25 (m, 18H), 6.91–6.87 (m, 4H), 6.11 (s, 2H), 4.00–3.85 (m, 8H) 1.73–1.00 (m, 24H) ppm; ^{19}F NMR (400 MHz, 298 K, $CDCl_3$) δ –136.90 (s, 2F), –157.83 (s, 1F), –163.69 (s, 2F) ppm; elemental analysis calc'd for $C_{78}H_{56}B_2F_{20}N_2O_6$ as a repeating unit: C, 61.68; H, 3.72; N, 1.84; found: C, 61.89; H, 4.71; N, 2.06; M_n 12000; M_w 22000; M_w/M_n 1.84 (estimated by SEC based on PEG standards); M_n 32000; M_w 57000; M_w/M_n 1.78 (estimated by SEC based on PS standards); T_{d5} 276 °C; T_{d10} 293 °C.

PEG-3: IR (NaCl) υ 2871, 1605, 1505, 1471, 1349, 1254, 1105, 969 cm^{-1}; ^1H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.97–7.26 (m), 6.96–6.93 (m), 6.13 (s), 4.13–3.43 (m, 4H), 1.49–1.05 (m) ppm; ^{19}F NMR (400 MHz, 298 K, $CDCl_3$) δ –136.64 (s, 2F), –157.49 (s, 1F), –163.55 (s, 2F) ppm; elemental analysis calc'd for $C_{160.8}H_{221.6}B_2F_{20}N_2O_{50.4}$ as a repeating unit: C, 56.96; H, 6.59; N, 0.83; found: C, 56.33; H, 6.82; N, 0.86; M_n 12000; M_w 29000; M_w/M_n 2.4 (estimated by SEC based on PEG standards); T_m 31.1 ºC; T_{d5} 270 ºC; T_{d10} 320 ºC.

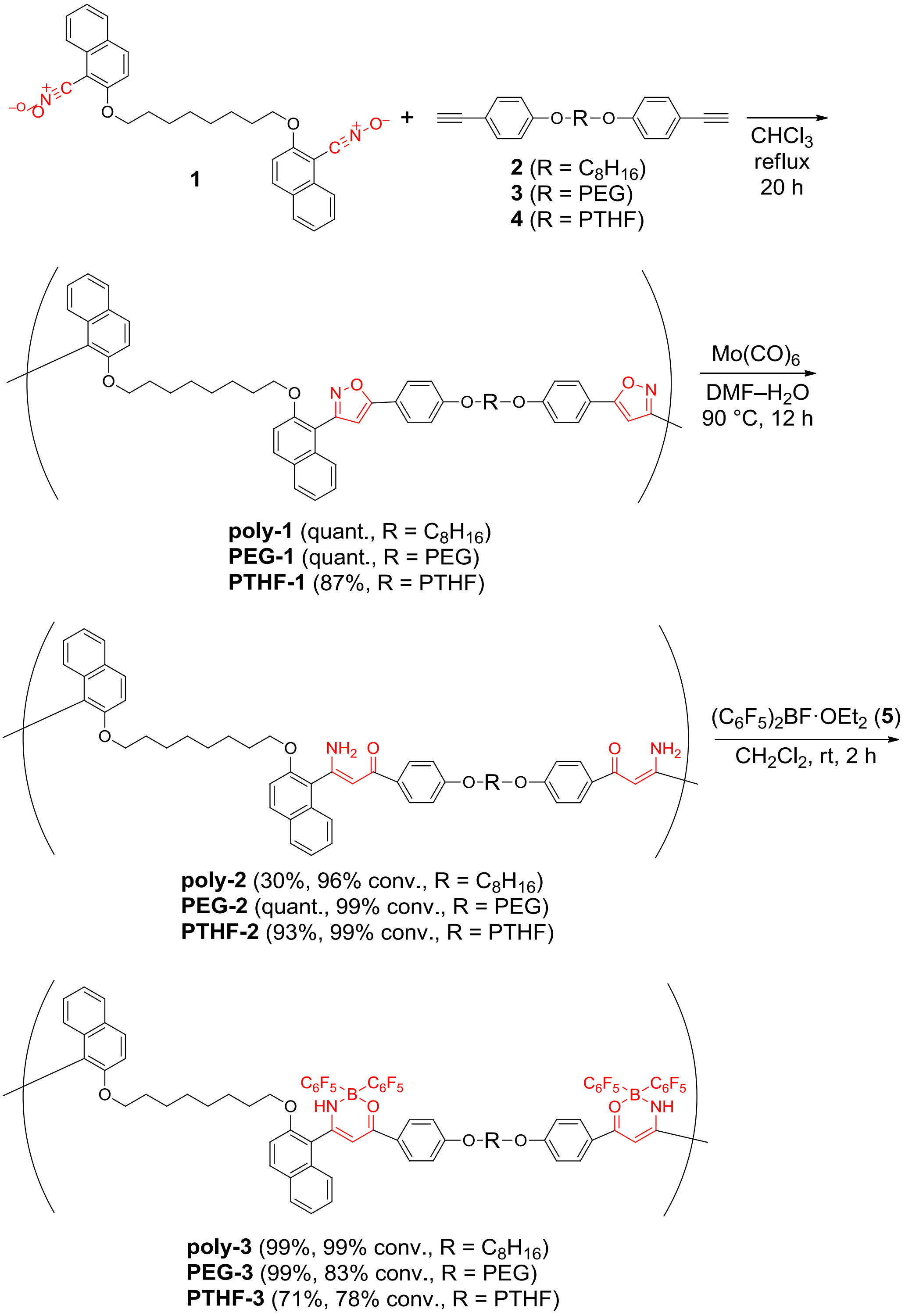
PTHF-3: IR (NaCl) υ 2940, 2857, 2359, 1606, 1508, 1466, 1368, 1250, 1112, 976 cm^{-1}; ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 8.00–7.27 (m), 6.94–6.88 (m), 6.12 (s), 4.08–3.95 (m), 3.66–3.51 (m, 4H), 3.25–3.22 (m), 1.98–1.56 (m, 4H), 1.56–1.00 (m) ppm; ^{19}F NMR (400 MHz, 298 K, $CDCl_3$) δ –136.64 (s, 2F), –157.50 (s, 1F), –163.60 (s, 2F) ppm; elemental analysis calc'd for $C_{230.9}H_{361.7}B_2F_{20}N_2O_{45.2}$ as a repeating unit: C, 64.64; H, 8.50; N, 0.65; found: C, 63.43; H, 8.82; N, 0.68; M_n 3500; M_w 7300; M_w/M_n 2.1 (estimated by SEC based on PSt standards); T_m 22.1 ºC; T_{d5} 267 ºC; T_{d10} 299 ºC.

Results and Discussion

Synthesis of Bis(nitrile N-oxide) ***1*** *and Poly(boron enaminoketonate)s*

Building upon our previous study,[24-36] we selected bis(2-alcoxy-naphthalene nitrile *N*-oxide) as a skeleton, speculating that it should serve well as a framework for a sufficiently-stabilized homoditopic nitrile *N*-oxide. Synthesis of the homoditopic nitrile *N*-oxide **1** was accomplished in 58% overall yield via a three-step reaction (Scheme 1, m.p. 119.5–120.7 °C). The structure of **1** was determined by ^{1}H NMR, ^{13}C NMR, IR, and FAB HRMS measurements.[37]

The polycycloaddition reactions of the homoditopic nitrile *N*-oxide **1** to model diyne **2** and polymeric diynes (**3** and **4**) were carried out in absence of a catalyst by heating in refluxing $CHCl_3$ for 12 h to give high molecular weight polyisoxazoles **poly-1**, **PEG-1**, and **PTHF-1**, respectively, in high yields (Scheme 2 and Table 1). One regioisomer was preferentially formed as confirmed by the ^{1}H NMR spectra.[16,17,37] Next, selective N–O bond cleavage of the isoxazole moiety in the resulting polyisoxazole was performed by using $Mo(CO)_6$[38,39] in a mixture of CH_3CN–DMF to give the corresponding poly(β-aminoenone) **poly-2**, **PEG-2**, and **PTHF-2** in high yields. From the integral ratio in the ^{1}H NMR spectra, it was found that almost 100% conversions of N–O cleavage reactions were achieved. Subsequent treatment of poly(β-aminoenone) with $(C_6F_5)_2BF\cdot OEt_2$ afforded **PBEK**s (**poly-3**, **PEG-3**, and **PTHF-3**) in high yields. The structures of **PBEK**s were determined by ^{1}H NMR, IR, and ^{19}F NMR spectra. The conversions of each polymer reaction were estimated to be high by the results of elemental analyses. The high reaction efficiencies from polyisoxazole to **PBEK**s emphasize the usefulness of nitrile *N*-oxide-based click polymer synthesis. The molecular weights of all polymers were evaluated by SEC analysis (Table 1). The M_w and M_w/M_n values of polyisoxazoles and PBEKs are approximately corresponding, indicating that the sequence of modification of polyisoxazole efficiently proceeded without degradation of the trunk polymer.[37] On the other hand, the M_w and M_w/M_n values of poly(β-aminoenone)s are contradictory to the others. Although the precise reason is not clear, the discrepant values may be attributed to a partial interchain aggregation of the β-aminoenone moieties and/or a strong interaction between the β-aminoenone moieties and the SEC stationary phase.



Scheme 2 Synthesis of polyisoxazoles and its transformation to **PBEK**s.

Table 1 Molecular weights of the resulting polymers.

Polyisoxazole	M_w	$M_\mathrm{w}/M_\mathrm{n}$
poly-1	51000[a]	1.7[a]
PEG-1	25000[b]	1.6[b]
PTHF-1	12000[a]	1.7[a]
Poly(β-aminoenone)	M_w	$M_\mathrm{w}/M_\mathrm{n}$
poly-2	24000[a]	1.5[a]
PEG-2	27000[b]	2.8[b]
PTHF-2	44000[a]	5.6[a]
PBEK	M_w	$M_\mathrm{w}/M_\mathrm{n}$
poly-3	57000[a]	1.8[a]
PEG-3	29000[b]	2.4[b]
PTHF-3	7300[a]	2.1[a]

[a] Estimated by SEC analysis on the basis of PSt standards (eluent: DMF). [a] Estimated by SEC analysis on the basis of PEG standards (eluent: DMF).

Table 2 summarizes the thermal properties of the resulting polymers. All polyisoxazoles and **PBEK**s, except for **poly-3,** are crystalline polymers, as suggested by the observed melting temperatures.[16] The crystallinity can be attributed to the interaction between the aromatic groups in the polymer main chain. The thermal decomposition temperatures were sufficiently high, thereby indicating the stability of the resulting polymers.

Table 2 Thermal properties of the resulting polymers.

polymer	T_m /°C[a]	T_{d5} /°C[b]
poly-1	90.3	323
PEG-1	38.9	277
PTHF-1	24.9	269
poly-3	–$^{\circ}$	276
PEG-3	31.1	270
PTHF-3	22.1	267

[a] Melting temperature measured by differential scanning calorimetry (DSC). [b] 5% Weight-loss temperature measured by thermogravimetric analysis (TGA). [c] Not observed.

Figure 2 shows the UV–vis and fluorescent spectra of the **PBEK**s in CH_2Cl_2 solution. Table 3 summarizes the results. Absorption maximum on the three UV–vis spectra appears at almost the same wavelength region with high a molar absorption coefficient (ε) of approximately 380–389 nm (Table 3). The Stokes shifts were sufficiently high, thereby suggesting good applicability of boron enaminoketonate skeleton to molecular probes.

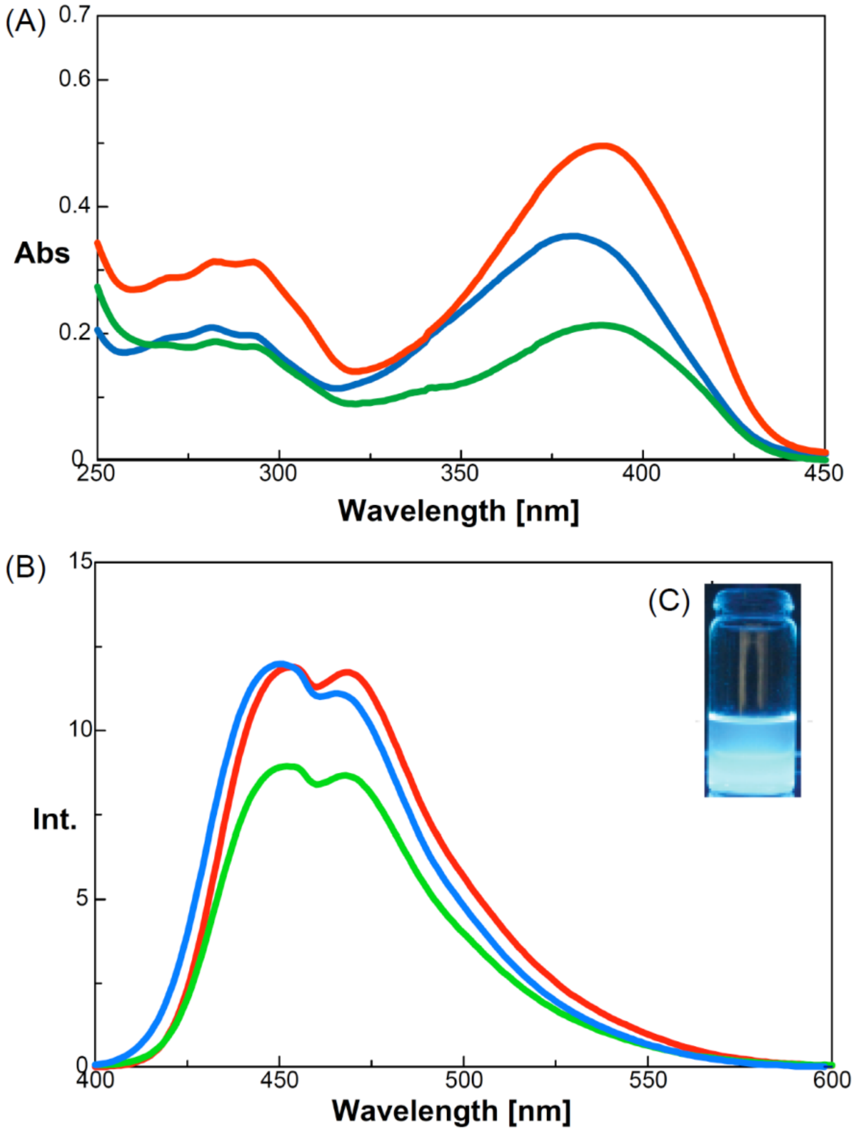


Figure 2 UV-vis (A) and fluorescent spectra (B) of **poly-3** (red line), **PEG-3** (blue line), and **PTHF-3** (green line) (20 μM in CH_2Cl_2, 293 K), and photographs of CH_2Cl_2 solutions of **PEG-3** (C) under irradiation by 254 nm light.

The solutions of the polymers in CH_2Cl_2 exhibited photoluminescence spectra with emission maxima around 451–453 nm when excited at their absorption maxima. The fluorescence quantum yields (Φ_F) of **poly-3**, **PEG-3**, and **PTHF-3** were 0.04, 0.05, and 0.07, respectively.[40] The Φ_Fs are of approximately the same value as those of the poly(boron diketonate)s, as reported by Chujo *et al.*[10-12] To clarify the photophysical properties of **PBEK**s, the model compound **6** was prepared (Figure 3) and the UV-vis and fluorescence spectra were measured (see supporting information).[37] It turned out that the absorption maximum on the UV-vis spectrum of **6** appeared at 389 nm with high molar absorption coefficient ($\varepsilon = 1.9 \times 10^4\ \mathrm{M^{-1} \cdot cm^{-1}}$).

In addition, the emission maxima of **6** appeared at 452 nm and the fluorescence quantum yield (Φ_F) of **6** was 0.06.[37] Such photo-physical properties of **6** were in good accordance with those of **PBEK**s, suggesting that the neighboring chromophore (boron enaminoketonate skeleton and naphthyl) units within the **PBEK**s did not interact in the ground and excited states. In addition, it emphasizes that the sequential transformation of the polyisoxazole enables the efficient introduction of the boron enaminoketonate skeletons into the polymer framework.

Table 3 Photophysical properties of **poly-3**, **PEG-3**, and **PTHF-3**.

Polymer	$\lambda_{abs}{}^{a}$ /nm	ε^{b} / $M^{-1} \cdot cm^{-1}$	$\lambda_{em}{}^{\circ}$ /nm	Quantum yield (Φ_F)^{d}	Stokes shift^{e} /cm^{-1}
poly-3^{f}	388	2.6×10^4	453	0.04	1.5×10^5
poly-3^{g}	–	–	499	0.04	–
PEG-3^{f}	380	1.8×10^4	451	0.05	1.4×10^5
PEG-3^{g}	–	–	467	0.04	–
PTHF-3^{f}	389	1.1×10^4	452	0.07	1.6×10^5
6	389	1.9×10^4	452	0.06	1.6×10^5

[a] Absorption maximum. [b] Molar absorption coefficient. [c] Emission maximum excited at the absorption maximum. [d] Based on the fluorescent intensity of 9,10-diphenylanthracene as a reference standard.[11] [e] Estimated by using the absorption maximum of the UV-vis spectrum and the fluorescence maximum at the shorter wavelength region of the bimodal peak. [f] 20 μM, CH_2Cl_2, 293 K. [g] Solid state emission was estimated in an emulsion prepared by a mixture of cyclohexane and CH_2Cl_2 (25:2).

The electronic states of the model compound **6** were also investigated by density-functional theory (DFT) method at the B3LYP/6-31G level of the theory (Figure 3). HOMO and LUMO of **6** are mainly located on the π-orbital of the boron enamino ketonate moiety, indicating that the π–π* excited state of **6** occupies the lowest excited state.[11,15] Additionally, the naphthalene moiety of **6** hardly affected the π-extension of the emissive framework due to the distorted structure.

To evaluate the emission spectra of **PBEK**s in a solid state, we estimated the fluorescent spectra of **poly-3** and **PEG-3** in emulsion states. The emulsions were prepared by precipitation of a CH_2Cl_2 solution of the polymer into an excess amount of cyclohexane as a poor solvent. As a result, these spectra appeared as broad peaks originating from an aggregation of the polymer (Figure 4). Both Φ_Fs in a solid state were approximately the same as those in a solution state without collisional quenching of the excited state by π– π stacking.[41]

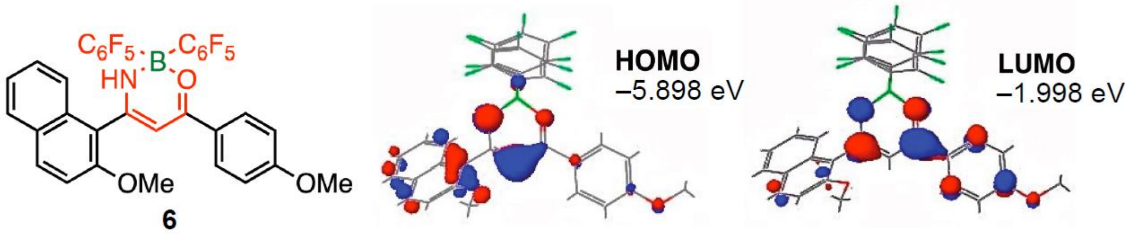


Figure 3. Structure and molecular orbital diagram for HOMO and LUMO of the model compound **6** estimated by DFT calculations (B3LYP/6-31G).

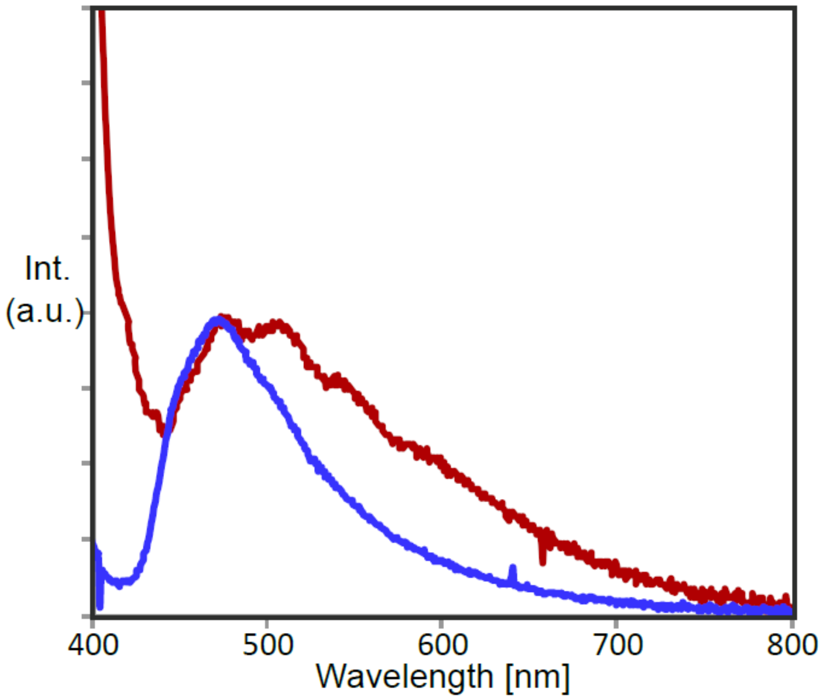


Figure 4. Fluorescent spectra (B) of **poly–3** (red line) and **PEG-3** (blue line) in solid states.

CONCLUSION

In conclusion, we have demonstrated first synthesis of **PBEK**s by exploiting stable homoditopic nitrile *N*-oxide **1** via a catalyst-free click polymerization and effective polymer transformations. Good optical properties such as large Stokes shift and Φ_Fs are the same as that of poly(boron diketonate), which indicates the usefulness of BEK skeleton as the substitute of boron diketonate. The outcome has broad applications not only to polymeric materials but also supramolecular chemistry because we have previously reported effective synthesis of rotaxane and polyrotaxane exploiting a cycloaddition of stable nitrile *N*-oxide.[16,27,30,33,36] The study of stimuli-responsive fluorescent switching system using BEK-containing supramolecular skeleton will be important for future.

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References

1 Halik, M. & Hartmann, H. Synthesis and characterization of new long-wavelength-absorbing oxonol dyes from the 2,2-difluoro-1,3,2-dioxaborine type. *Chem.–Eur. J.* **5**, 2511–2517 (1999).

2 Cogné-Laage, E., Allemand, J.-F., Ruel, O., Baudin, J.-B., Croquette, V., Blanchard-Desce, M. & Jullien, L. Diaroyl(methanato)boron difluoride compounds as medium-sensitive two-photon fluorescent probes. *Chem.–Eur. J.* **10**, 1445–1455 (2004).

3 Ono, K., Yoshikawa, K., Tsuji, Y., Yamaguchi, H., Uozumi, R., Tomura, M., Taga, K. & Saito, K. Synthesis and photoluminescence properties of BF_2 complexes with 1,3-diketone ligands. *Tetrahedron* **63**, 9354–9358 (2007).

4 Maeda, H., Mihashi, Y. & Haketa, Y. Heteroaryl-Substituted C_3-Bridged Oligopyrroles: Potential Building Subunits of Anion-Responsive π-Conjugated Oligomers. *Org. Lett.* **10**, 3179–3182 (2008).

5 Haugland, R. P. *The Handbook–A Guide to Fluorescent Probes and Labeling Technologies*, *10th ed.* (ed. Spence, M. T. Z.) Chapter 1, Section 1.4. (Molecular Probes: Eugene, OR, 2005).

6 Pavlopoulos, T. G., Boyer, J. H. & Sathyamoorthi, G. Laser action from a 2,6,8-position trisubstituted 1,3,5,7-tetramethylpyrromethene-BF_2 complex: part 3. *Appl. Opt.* **37**, 7797–7800 (1998).

7 Sanchez-Barragan, I., Costa-Fernandez, J. M., Sanz-Medel, A., Valledor, M. & Campo, J. C. Room-temperature phosphorescence (RTP) for optical sensing. *Trends Anal. Chem.* **25**, 958–967 (2006).

8 Galletta, M., Puntoriero, F., Campagna, S., Chiorboli, C., Quesada, M., Goeb, S. & Ziessel, R. Absorption Spectra, Photophysical Properties, and Redox Behavior of Ruthenium(II) Polypyridine Complexes Containing Accessory Dipyrromethene-BF_2 Chromophores. *J. Phys. Chem. A* **110**, 4348–4358 (2006).

9 Zhang, G., Chen, J., Payne, S. J., Kooi, S. E., Demas, J. N. & Fraser, C. L. Multi-Emissive Difluoroboron Dibenzoylmethane Polylactide Exhibiting Intense Fluorescence and Oxygen-Sensitive Room-Temperature Phosphorescence. *J. Am. Chem. Soc.* **129**, 8942–8943 (2007).

10 Nagai, A., Kokado, K., Nagata, Y. & Chujo, Y. 1,3-Diketone-Based Organoboron Polymers: Emission by Extending π-Conjugation along a Polymeric Ligand. *Macromolecules* **41**, 8295–8298 (2008).

11 Nagai, A., Kokado, K., Nagata, Y., Arita, M. & Chujo, Y. Highly Intense Fluorescent Diarylboron Diketonate. *J. Org. Chem.* **73**, 8605–8607 (2008).

12 Tanaka, K., Tamashima, K., Nagai, A., Okawa, T. & Chujo, Y. Facile Modulation of Optical Properties of Diketonate-Containing Polymers by Regulating Complexation Ratios with Boron. *Macromolecules* **46**, 2969–2975 (2013).

13 For a related study concerning synthesis and spectral study of fluorescent BF_2 complexes with 1,3-enaminoketone ligands, see; Xia, M., Wu, B. & Xiang, G. Synthesis, structure and spectral study of two types of novel fluorescent BF_2 complexes with heterocyclic 1,3-enaminoketone ligands. *J. Fluorine Chem.* **129**, 402–408 (2008).

14 Macedo, F. P., Gwengo, C., Lindeman, S. V., Smith, M. D. & Gardinier, J. R. β-diketonate, β-ketoiminate, and β-diiminate complexes of difluoroboron. *Eur. J. Inorg. Chem.* **2008**, 3200–3211 (2008).

15 Yoshii, R., Nagai, A., Tanaka, K. & Chujo, Y. Highly Emissive Boron Ketoiminate Derivatives as a New Class of Aggregation-Induced Emission Fluorophores. *Chem.–Eur. J.* **19**, 4506–4512 (2013).

16 Koyama, Y., Matsumura, T., Yui, T., Ishitani, O. & Takata, T. Fluorescence Control of Boron Enaminoketonate Using a Rotaxane Shuttle. *Org. Lett.* **15**, 4686–4689 (2013).

17 Lee, Y.-G., Koyama, Y., Yonekawa, M. & Takata, T. New Click Chemistry: Polymerization Based on 1,3-Dipolar Cycloaddition of a Homo Ditopic Nitrile *N*-Oxide and Transformation of the Resulting Polymers into Reactive Polymers. *Macromolecules* **42**, 7709–7717 (2009).

18 Koyama, Y., Seo, A. & Takata, T. Polymer modification exploiting stable nitrile *N*-oxide. *Nippon Gomu Kyokaishi* **84**, 111–116 (2011).

19 M. Cai, J. Sha & Q. Xu, MCM-supported bidentate phosphine palladium(0) complex: a highly active and recyclable catalyst for the Sonogashira reaction of aryl iodides. *Tetrahedron*, **63**, 4642–4647 (2007).

20 J. Yoshino, N. Kano & T. Kawashima, Synthesis of the most intensely fluorescent azobenzene by utilizing the B-N interaction. *Chem. Commun.* **43**, 559–561 (2007).

21 R. Duchateau, S. J. Lancaster, M. Thornton-Pett & M. Bochmann, Synthesis of Cyclopentadienyl-, Indenyl-, and Fluorenylbis(pentafluorophenyl)boranes as Ligands in Titanium and Zirconium Half-Sandwich Complexes. The Crystal Structures of $[C_{13}H_9B(C_6F_5)_2 \cdot t\text{-BuNH}_2]$, $[C_{13}H_8SiMe_3B(C_6F_5)_2]$, and $\{\eta_5\text{-}C_5H_4B(C_6F_5)_2\}TiCl_3$. *Organometallics*, **16**, 4995–5005 (1997).

22 T. Hirose & K. Matsuda, Self-assembly of amphiphilic fluorescent dyes showing aggregate-induced enhanced emission: temperature dependence of molecular alignment and intermolecular interaction in aqueous environment. *Chem. Commun.*, **45**, 5832–5834 (2009).

23 Pirali, T., Gatti, S., Di Brisco, R., Tacchi, S., Zaninetti, R., Brunelli, E., Massarotti, A., Sorba, G., Canonico, P. L., Moro, L., Genazzani, A. A., Tron, G. C. & Billington, R. A. Hybrid nanoparticles with CO_2-responsive shells and fluorescence-labelled magnetic cores. *Chem. Med. Chem.* **2**, 437–440 (2007).

24 Koyama, Y., Yonekawa, M. & Takata, T. New click chemistry: click polymerization via 1,3-dipolar addition of homo-ditopic aromatic nitrile oxides formed in situ. *Chem. Lett.* **37**, 918–919 (2008).

25 Lee, Y.-G., Yonekawa, M., Koyama, Y. & Takata, T. Synthesis of a kinetically stabilized homoditopic nitrile *N*-oxide directed toward catalyst-free click polymerization. *Chem. Lett.* **39**, 420–421 (2010).

26 Lee, Y.-G., Koyama, Y., Yonekawa, M. & Takata, T. Synthesis of Main-Chain-Type Polyrotaxanes by New Click Polymerization Using Homoditopic Nitrile *N*-Oxides via Rotaxanation-Polymerization Protocol. *Macromolecules* **43**, 4070–4080 (2010).

27 Matsumura, T., Ishiwari, F., Koyama, Y. & Takata, T. C-C Bond-Forming Click Synthesis of Rotaxanes Exploiting Nitrile *N*-Oxide. *Org. Lett.* **12**, 3828–3831 (2010).

28 Koyama, Y. & Takata, T. Polymer synthesis exploiting nitrile *N*-oxide. *Kobunshi Ronbunshu* **68**, 147–159 (2011).

29 Yonekawa, M., Koyama, Y., Kuwata, S. & Takata, T. Intramolecular 1,3-dipolar cycloaddition of nitrile *N*-oxide accompanied by dearomatization. *Org. Lett.* **14**, 1164–1167 (2012).

30 Jang, K., Miura, K., Koyama, Y. & Takata, T. Catalyst- and Solvent-Free Click Synthesis of Cyclodextrin-Based Polyrotaxanes Exploiting a Nitrile *N*-Oxide. *Org. Lett.* **14**, 3088–3091 (2012).

31 Koyama, Y., Miura, K., Cheawchan, S., Seo, A. & Takata, T. Cascade functionalization of unsaturated bond-containing polymers using ambident agents possessing both nitrile *N*-oxide and electrophilic functions. *Chem. Commun.* **48**, 10304–10306 (2012).

32 Koyama, Y., Wang, C., Miura, K., Cheawchan, S., Seo, A. & Takata, T. Development of nitrile *N*-oxide agents directed toward catalyst-free solid-state modification of common polymers. *Hyomen* **50**, 228–238 (2012).

33 Iguchi, H., Uchida, S., Koyama, Y. & Takata, T. Polyester-Containing α-Cyclodextrin-Based Polyrotaxanes: Synthesis by Living Ring-Opening Polymerization, Polypseudorotaxanation, and End Capping Using Nitrile *N*-Oxide. *ACS Macro Lett.* **2**, 527–530 (2013).

34 Wang, C., Koyama, Y., Yonekawa, M., Uchida, S. & Takata, T. Polymer nitrile *N*-oxides directed toward catalyst- and solvent-free click grafting. *Chem. Commun.* **49**, 7723–7725 (2013).

35 Cheawchan, S., Koyama, Y., Uchida, S. & Takata, T. Catalyst-free click cascade functionalization of unsaturated-bond-containing polymers using masked-ketene-tethering nitrile *N*-oxide. *Polymer*, **54**, 4501–4510 (2013).

36 Yuki, T., Koyama, Y., Matsumura, T. & Takata, T. Click Annulation of Pseudo[2]rotaxane to [2]Catenane Exploiting Homoditopic Nitrile *N*-Oxide. *Org. Lett.* **15**, 4438–4441 (2013).

37 See, Supplementary Materials.

38 Nitta, M. & Higuchi, T. $Mo(CO)_6$-induced N-O cleavage of isoxazoles. A convenient route to pyridine-4(1*H*)-ones. *Heterocycles* **38**, 853–857 (1994).

39 Li, C.-S. & Lacasse, E. Synthesis of pyran-4-ones from isoxazoles. *Tetrahedron Lett.* **43**, 3565–3568 (2002).

40 Ishida, H., Tobita, S., Hasegawa, Y., Katoh, R. & Nozaki, K. Recent advances in instrumentation for absolute emission quantum yield measurements. *Coord. Chem. Rev.* **254**, 2449–2458 (2010).

41 Sato, T., Jiang, D.-L. & Aida, T. A Blue-Luminescent Dendritic Rod: Poly(phenyleneethynylene) within a Light-Harvesting Dendritic Envelope. *J. Am. Chem.*

Soc. **121**, 10658–10659 (1999).

Scheme Legends

Scheme 1 Synthesis of homoditopic nitrile *N*-oxide **1**.

Scheme 2 Synthesis of polyisoxazoles and its transformation to **PBEK**s.

Figure Legends

Figure 1 Click polymerization utilizing a homoditopic nitrile *N*-oxide with a diyne, and the transformation of a polyisoxazole into fluorescent **PBEK**.

Figure 2 UV-vis (A) and fluorescent spectra (B) of **poly-3** (red line), **PEG-3** (blue line), and **PTHF-3** (green line) (20 μM in CH_2Cl_2, 293 K), and photographs of CH_2Cl_2 solutions of **PEG-3** (C) under irradiation by 254 nm light.

Figure 3 Structure and molecular orbital diagram for HOMO and LUMO of the model compound **6** estimated by DFT calculations (B3LYP/6-31G).

Figure 4 Fluorescent spectra (B) of **poly–3** (red line) and **PEG-3** (blue line) in solid states.

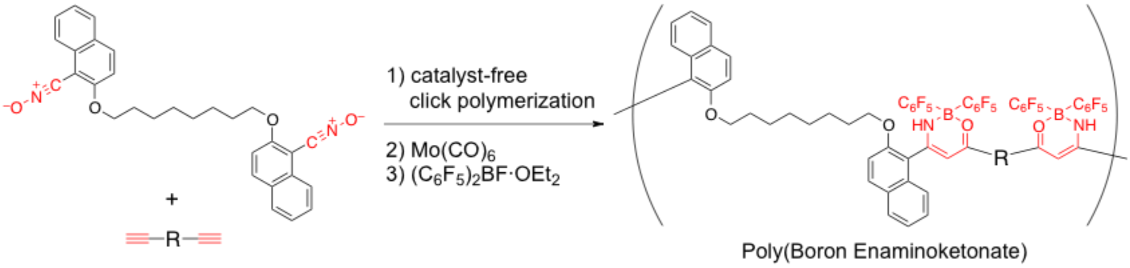
Table Legends

Table 1 Molecular weights of the resulting polymers.

Table 2 Thermal properties of the resulting polymers.

Table 3 Photophysical properties of **poly-3**, **PEG-3**, and **PTHF-3**.

Graphical Abstract



Fluorescent poly(boron enaminoketonate)s (**PBEK**s) were synthesized via polycycloaddition of homoditopic nitrile *N*-oxide to diynes and subsequent polymer reactions. Click polycycloaddition of the nitrile *N*-oxide to various diynes effectively produced polyisoxazoles in high yields. Transformation of the polyisoxazoles afforded the corresponding fluorescent **PBEK**s via intermediary formation of poly(β-aminoenone) followed by the reaction with $(C_6F_5)_2BF\cdot OEt_2$. The optical properties of **PBEK**s were evaluated by the UV–vis and fluorescent spectra obtained under solution and solid states.