Supporting Information

Synthesis and Photophysical Properties for Water-soluble Fluorinated Poly(aryleneethynylene)s

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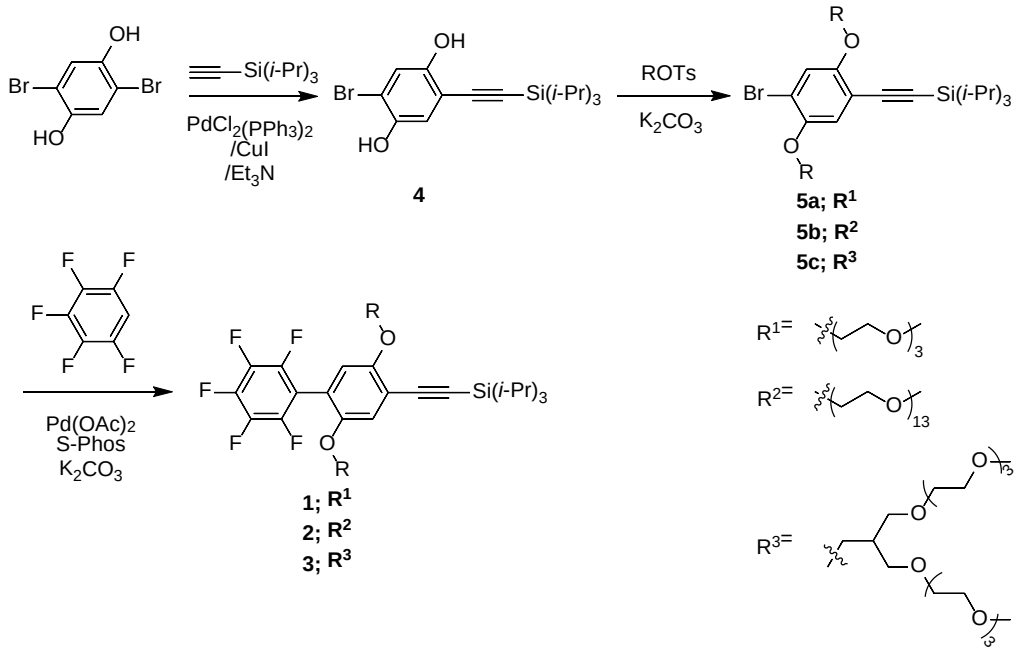
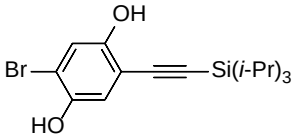
General procedure of Syntheses of monomers

Scheme S1. Synthetic route for the monomers 1-3

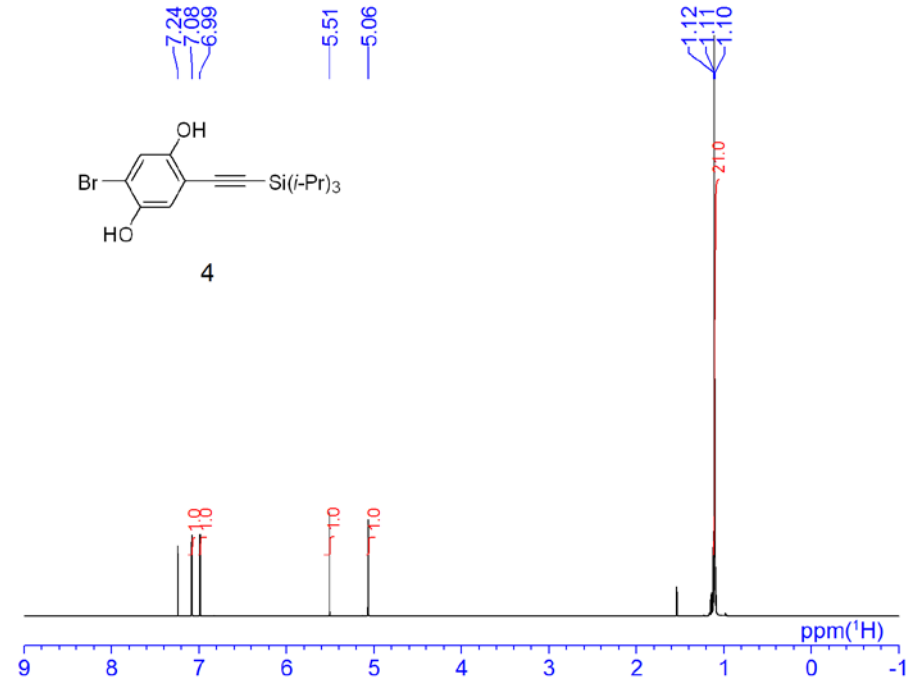




Synthesis of 4

In a reaction flask under Ar, 2,5-dibromohydroquinone (26.78 g 100 mmol), CuI (380.10 mg, 2.00 mmol), $PdCl_2(PPh_3)_2$ (701.90 mg, 1.00 mmol), DMF (120 mL) and triethylamine (120 mL) were added. Triisopropylsilylacetylene was then added, and the mixture was stirred at 50 °C for 48 h. To the mixture was added a saturated aqueous solution of NH_4Cl and the resulting mixture was extracted with chloroform. The organic layer was washed with a saturated aqueous solution of NaCl and dried over anhydrous Na_2SO_4. After filtration and removal of the solvent, the residue was purified with column chromatography using silica gel (hexane/chloroform = 3/1) to give the title compound as a pale yellow powder (7.95 g, 21.5 mmol, 22%). A pale yellow powder: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.09-1.15 (m, 21H), 5.06 (s, 1H), 5.51 (s, 4H), 6.99 (s, 1H), 7.08 (s, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 11.3, 18.9, 100.0, 100.3, 110.6, 112.1, 117.8, 145.9, 151.5; HRMS (FAB, matrix = 3-nitrobenzyl alcohol, NBA) calcd for $C_{17}H_{25}BrO_2Si$ ($[M]^+$) *m*/*z* 368.0807, found 368.0803.

a)



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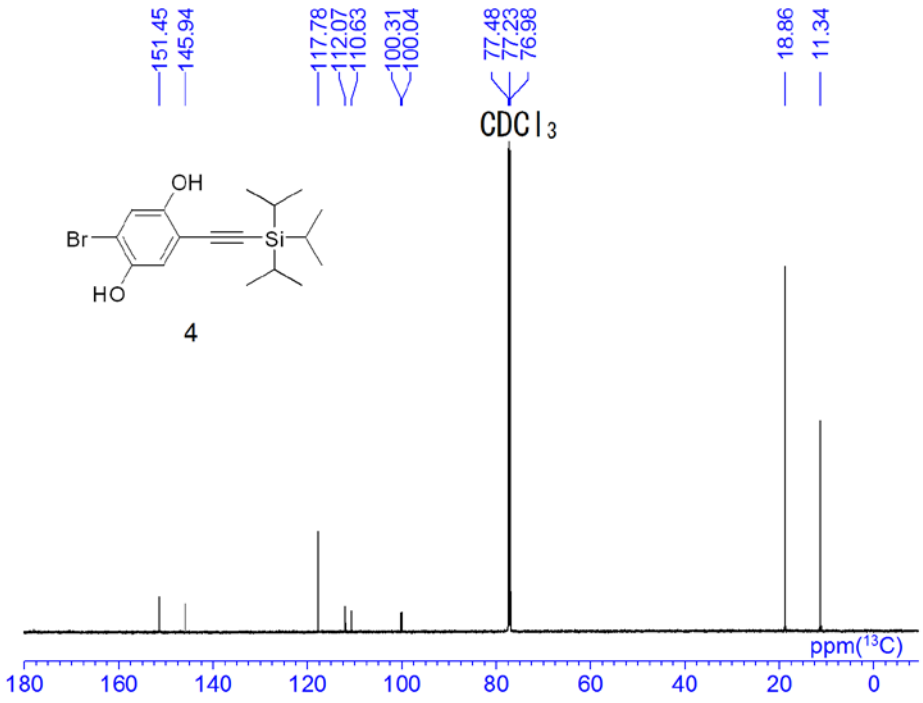
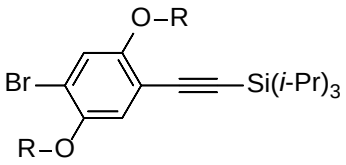


Figure S1. a) ^{1}H and b) ^{13}C NMR spectra of **4** ($CDCl_3$)

Synthesis of 5a-c



5a; R^1
5b; R^2
5c; R^3

ROTs was synthesized according to the modified procedure reported previously.[1, 2] R^2OH (UNIOX M-550, average molecular weight was determined by H^1 NMR) was provided by NOF Corporation.

5a

In a reaction flask under Ar, **4** (2.40 g, 6.50 mmol), R^1OTs (4.20 g, 13.2 mmol), K_2CO_3 (8.72 g, 63.1 mmol), DMF (72 mL) and were added. The mixture was stirred at 80 °C for 19 h. To the mixture was added a saturated aqueous solution of NaCl and the resulting mixture was extracted with chloroform and dried over anhydrous Na_2SO_4. After filtration and removal of the solvent, the residue was purified with column chromatography using silica gel (hexane/ethylacetate = 1/1) and aluminum oxide (acetone) to give the title compound (3.85 g, 5.81 mmol, 89%) as a color less oil. A colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.10 (s, 21H), 3.35-3.86 (m, 26H), 4.08-4.12 (m, 4H), 6.95 (s, 1H), 7.06 (s, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 11.5, 18.9, 59.2, 69.5, 69.8(76), 69.8(83), 70.2, 70.7, 70.8, 70.9, 71.1, 71.2, 72.1(11), 72.1(12), 96.1, 102.4, 113.3, 113.6, 118.4, 119.1, 149.6, 154.9; HRMS (FAB, matrix = 3-nitrobenzyl alcohol, NBA) calcd for $C_{31}H_{53}BrO_8Si$ ($[M]^+$) *m*/*z* 660.2693, found 660.2675.

5b

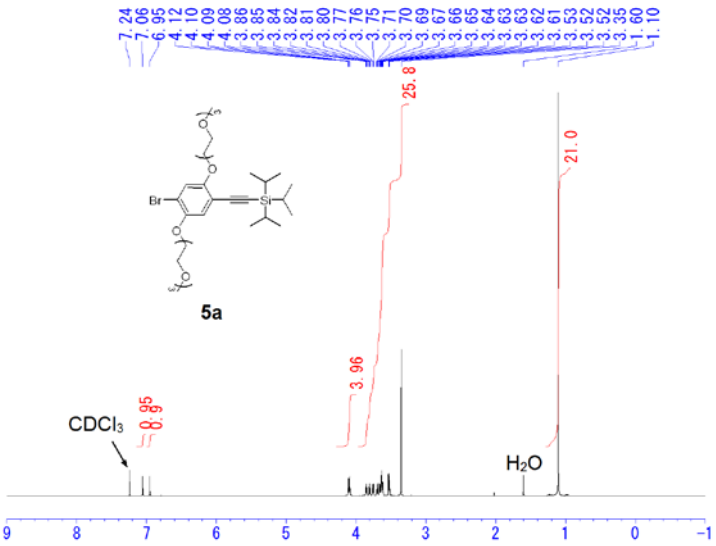
In a reaction flask under Ar, **4** (2.40 g, 6.50 mmol), R^2OTs (5.91 g, 8.40 mmol), K_2CO_3 (5.40 g, 39.07 mmol), DMF (45 mL) and were added. The mixture was stirred at 80 °C for 40 h. To the mixture was added a saturated aqueous solution of NaCl and the resulting mixture was extracted with chloroform and dried over anhydrous Na_2SO_4. After filtration and removal of the solvent, the residue was purified with column chromatography using aluminum oxide (acetone) and preparative GPC (chloroform) to give the title compound (4.81 g, 3.28 mmol, 81%) as a colorless oil. A colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.10 (s, 21H), 3.35-3.85 (m, 101H), 4.07-4.10 (m, 4H), 6.94 (s, 1H), 7.05 (s, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 11.5, 18.9, 59.2, 69.5, 69.8(76), 69.8(83), 70.2, 70.7-70.8 (m), 70.9, 71.1, 71.2, 72.1, 96.2, 102.4, 113.3, 113.6, 118.4, 119.0, 149.6, 155.0; (MALDI-TOF-MS, matrix = dithranol) calcd for $C_{53}H_{97}BrO_{18}Si$ ($[M+Na]^+$) *m*/*z* 1563.7834, 1564.7867, 1565.7813, 1566.7847, 1567.7880 found 1563.2694, 1564.2718, 1565.2630, 1566.2679, 1567.2603

5c

In a reaction flask under Ar, **4** (500 mg, 1.35 mmol), R^3OTs (1.55 g, 2.8 mmol), K_2CO_3 (1.8 g, 13.0 mmol), DMF (15 mL) and were added. The mixture was stirred at 80 °C for 48 h. To the mixture was added a saturated aqueous solution of NaCl and the resulting mixture was extracted

with chloroform and dried over anhydrous $MgSO_4$. After filtration and removal of the solvent, the residue was purified with column chromatography using silica gel (chloroform/methanol = 100/1) to give the title compound (1.09 g, 0.96 mmol, 71%) as a colorless oil. A colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.1-1.15 (m, 21H), 2.34-2.43(m, 2H), 3.35-3.62 (m, 68H), 3.98-4.01 (m, 4H), 6.91 (s, 1H), 7.03 (s 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 11.5, 18.9, 40.1, 40.2, 59.2, 67.2, 68.0, 69.3, 69.4, 70.6-70.8 m, 72.1, 95.6, 102.5, 112.5, 113.4, 117.0, 118.3, 149.1, 154.8; HRMS (FAB, matrix = 3-nitrobenzyl alcohol, NBA) calcd for $C_{53}H_{97}BrO_{18}Si$ ($[M]^+$) *m/z* 1128.5628, found 1128.5634.

a)



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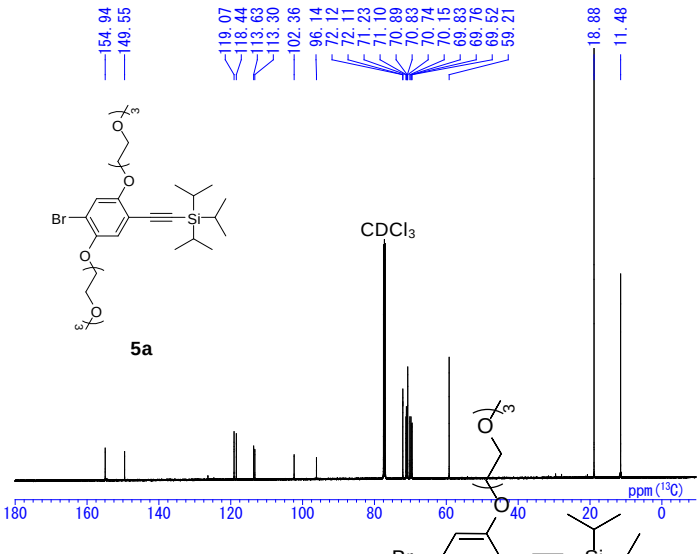
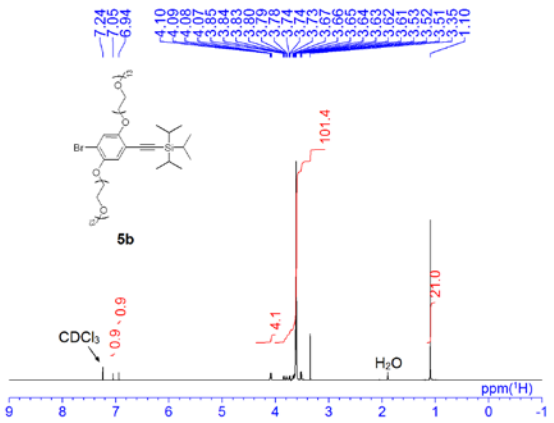


Figure S2. a) ^{1}H and b) ^{13}C NMR spectra of **5a** ($CDCl_3$).

a)



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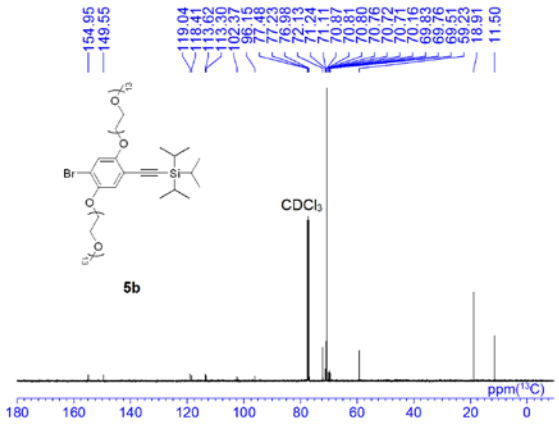

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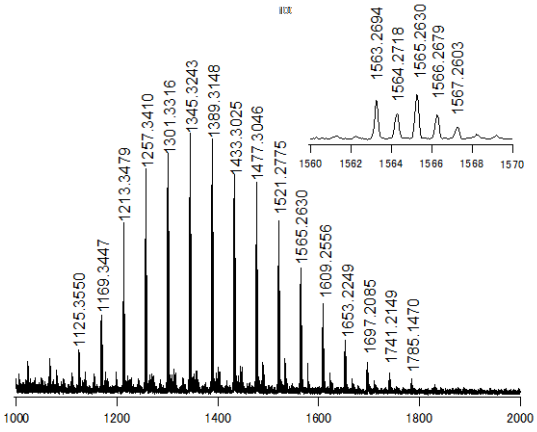
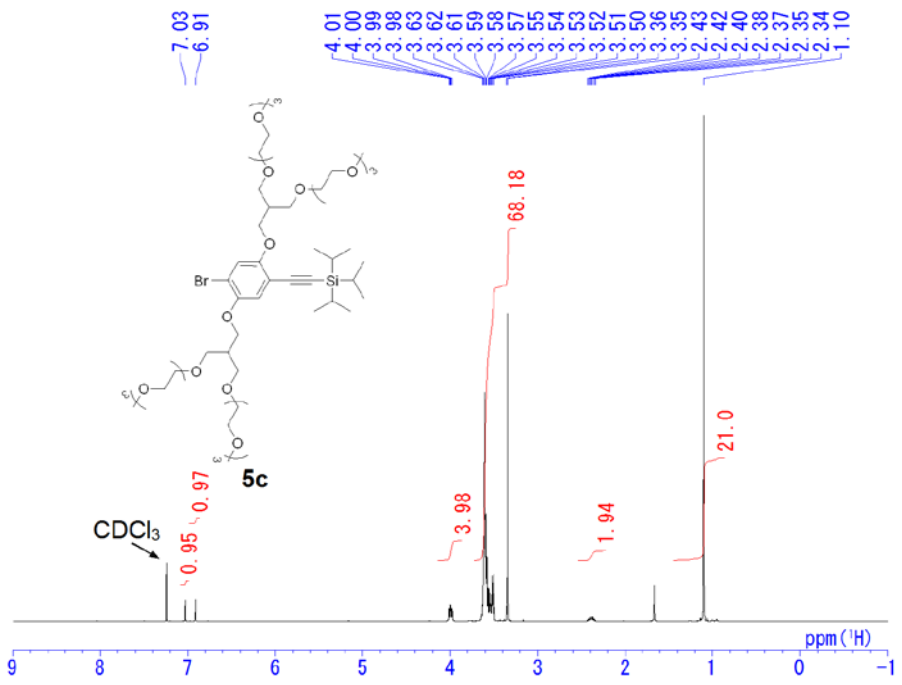


Figure S3. a) ^{1}H NMR ($CDCl_3$), b) ^{13}C NMR ($CDCl_3$), and c) MALDI-TOF-MS spectra of **5b**.

a)



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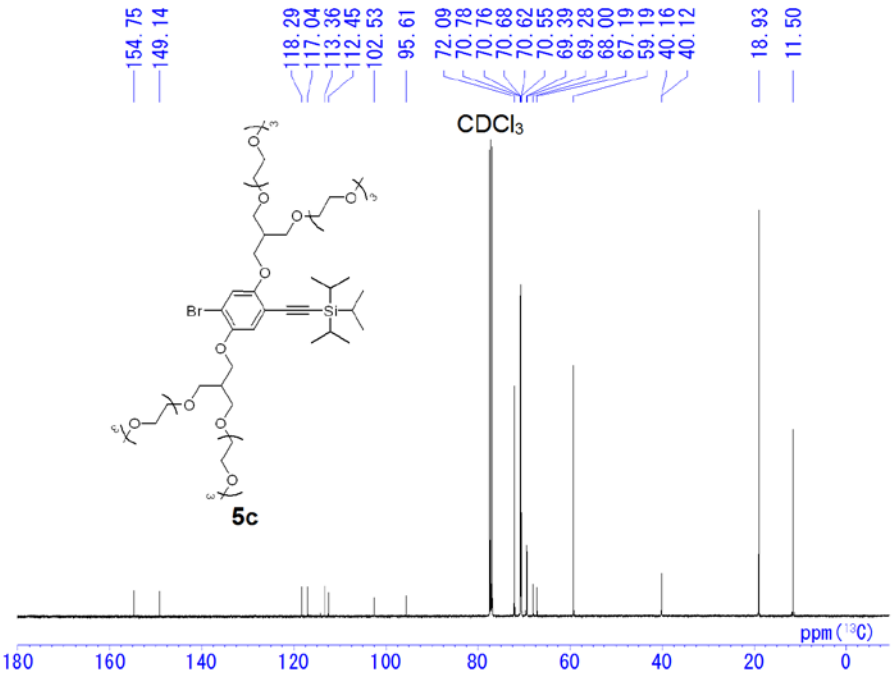

Figure S4. a) ^{1}H and b) ^{13}C NMR spectra of **5c** ($CDCl_3$).

Synthesis of monomer 1

In a reaction flask under Ar, **5a** (3.7 g, 5.24 mmol), $Pd(OAc)_2$ (52.3 mg, 0.233 mmol), 2-cyclohexylphosphino-2',6'-dimethoxy-1,1'-biphenyl (191.6 mg, 0.466 mmol), K_2CO_3 (1.35 g, 9.80 mmol), and isopropylacetate (14 mL) were added. Pentafluorobenzene (2.77 g, 16.52 mmol) was then added, and the mixture was stirred at 80 °C for 36 h. The mixture was purified with column chromatography using silica gel (hexane/ethylacetate = 7/1, 5/1, 3/1, and 1/1) to give the title compound (3.47 g, 4.64 mmol, 83%) as a pale yellow oil. A pale yellow oil: ^{1}H NMR (500MHz, $CDCl_3$) δ 1.12 (s, 21H), 3.34-3.83 (m, 26H), 4.07-4.13 (m, 4H), 6.74 (s, 1H), 7.07 (s, 1H); $^{13}C\{^1H\}$ NMR (125MHz, $CDCl_3$) δ 11.5, 18.9, 59.2, 69.1, 69.5, 69.7, 69.9, 70.7-70.8 (m), 70.9(87), 70.9(92), 71.1, 72.1(10), 72.1(12), 96.9, 102.5, 115.9, 116.7, 118.2, 150.5, 154.4; $^{19}F\{^1H\}$ NMR (471 MHz, $CDCl_3$) δ –163.0 (td, J_F=21.7, 7.8 Hz, 2F), –155.5 (t, J_F= 21.7 Hz, 1F), –139.7 (td, J_F= 21.7 Hz, 7.8 Hz, 2F); HRMS (FAB, matrix = 3-nitrobenzyl alcohol, NBA) calcd for $C_{37}H_{53}F_5O_8Si$ ($[M]^+$) *m*/*z* 748.3430, found 748.3456.

Synthesis of monomer 2

In a reaction flask under Ar, **5b** (4.4 g, 2.73 mmol), $Pd(OAc)_2$ (213 mg, 0.950 mmol), 2-cyclohexylphosphino-2',6'-dimethoxy-1,1'-biphenyl (780 mg, 1.9 mmol), K_2CO_3 (829 mg, 6.00 mmol), and isopropylacetate (9 mL) were added. Pentafluorobenzene (1.51 g, 9.00 mmol) was then added, and the mixture was stirred at 80 °C for 36 h. The mixture was purified with column chromatography using silica gel (methanol/chloroform = 0, 1/100, and 3/200) to give the title compound (2.93 g, 0.87 mmol, 63%) as a pale yellow oil. A pale yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.12 (s, 21H), 3.35-3.82 (m, 100H), 4.12-4.06 (m, 4H), 6.74 (s, 1H), 7.06 (s, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 11.5, 18.9, 59.2, 69.1, 69.5, 69.7, 69.9, 70.7-70.9 (m), 71.1, 72.1, 96.9, 102.5, 115.9, 116.7, 118.2, 150.4, 154.4; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ –163.17 (td, J_F = 21.8, 8.2 Hz, 2F), –155.67 (t, J_F = 21.8 Hz, 1F), –139.86 (td, J_F = 21.8 Hz, 8.2 Hz, 2F)

Synthesis of monomer 3

In a reaction flask under Ar, **5c** (1.08 g, 0.93 mmol), $Pd(OAc)_2$ (65.1 mg, 0.290 mmol), 2-cyclohexylphosphino-2',6'-dimethoxy-1,1'-biphenyl (238.11 mg, 0.580 mmol), K_2CO_3 (276.4 mg, 2.00 mmol), and isopropylacetate (2.8 mL) were added. Pentafluorobenzene (504.22 mg, 2.71 mmol) was then added, and the solution was stirred at 80 °C for 40 h. The mixture was purified with column chromatography using silica gel (methanol/chloroform = 0 and 1/100) to give title compound (1.05 g, 0.87 mmol, 91%) as a pale yellow oil. A pale yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.13 (s, 21H), 1.57 (s, 4H), 3.34-3.64 (m, 68H), 3.98 (m, 4H), 6.71 (s, 1H-) 7.05 (s, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 11.5, 18.9, 39.9, 40.2, 59.1, 67.1, 69.2, 69.3, 70.5-70.7 (m), 72.0, 96.3, 102.6, 115.0-115.1 (m), 116.0, 117.4, 149.9, 154.2; $^{19}F\{^1H\}$ NMR (471 MHz, $CDCl_3$) δ –162.9 (td, J_F=21.7, 7.8 Hz, 2F), –155.3 (t, J_F= 21.7 Hz, 1F), –139.5 (td, J_F= 21.7 Hz, 7.8 Hz, 2F); HRMS (FAB, matrix = 3-nitrobenzyl alcohol, NBA) calcd for $C_{59}H_{97}F_5O_{18}Si$ ($[M]^+$) *m*/*z* 1651.8571, 1652.8604, 1653.8638, 1654.8671, found 1651.3214, 1652.3350, 1653.3207, 1654.4209.

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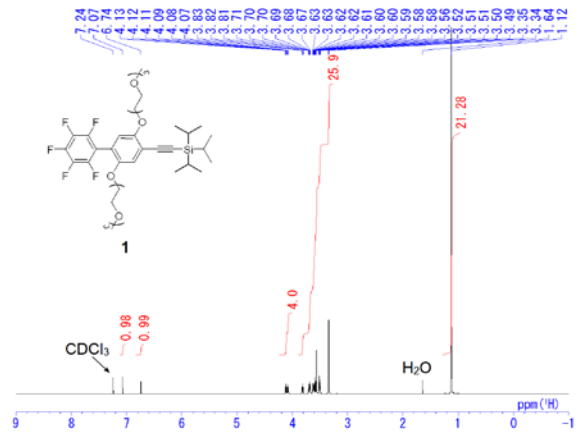

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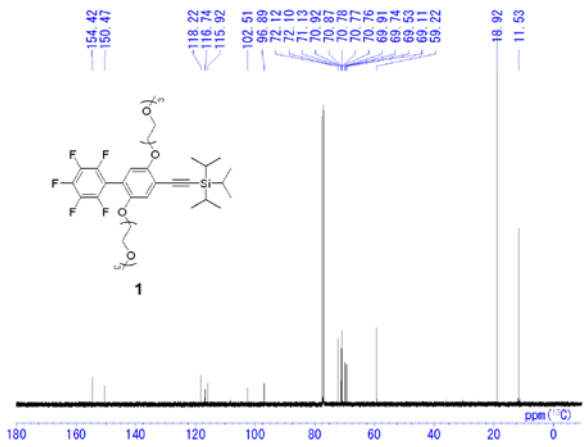

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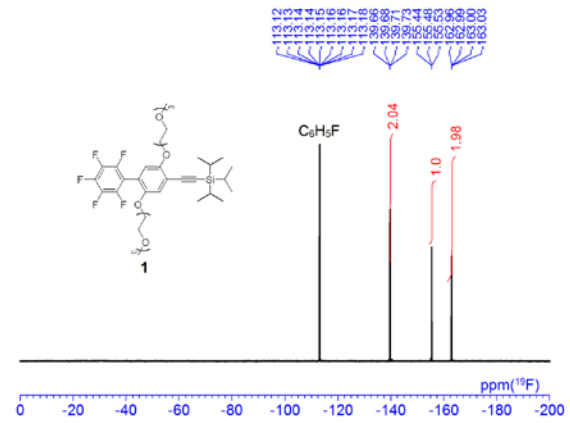

Figure S5. a) ^{1}H, b) ^{13}C, and c) ^{19}F NMR spectra of **1** ($CDCl_3$).

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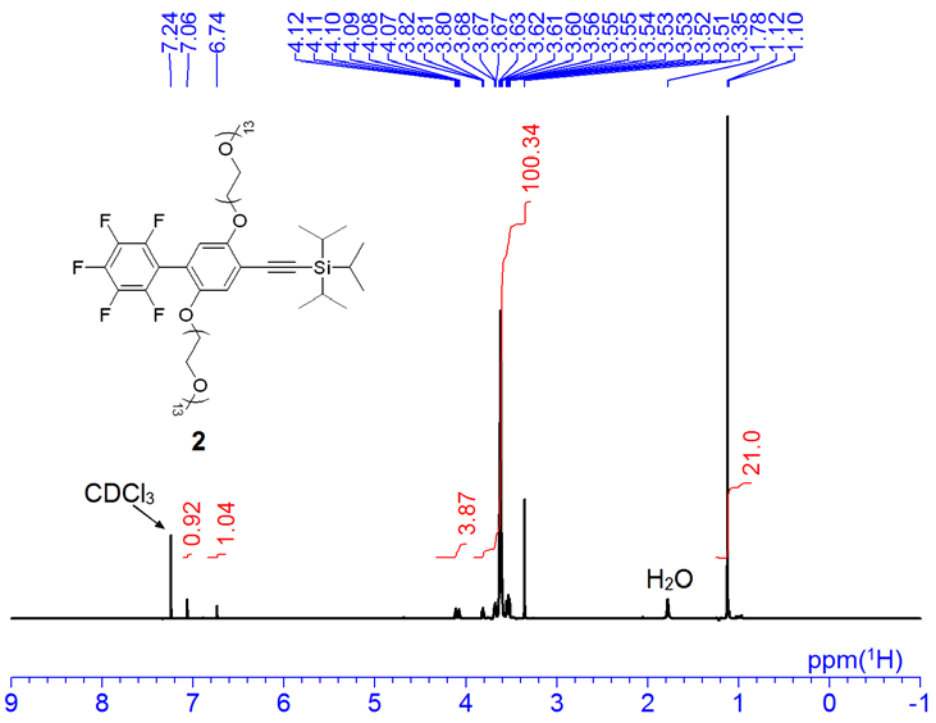
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3.54
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3.53
3.52
3.51
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1.12
1.10
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6
5
4
3
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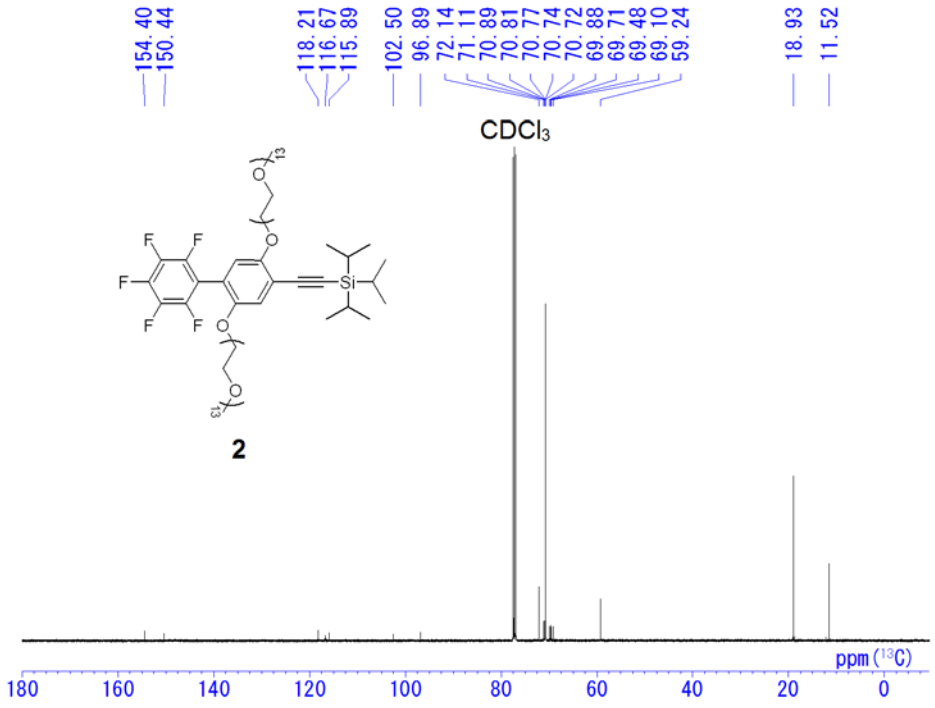
1
0
-1

b)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100
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60
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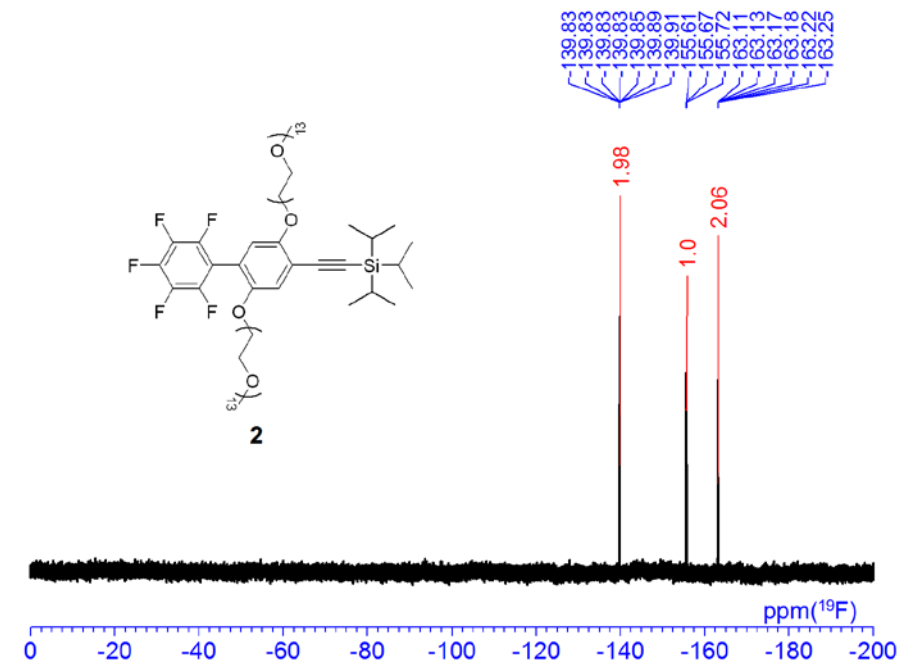
0

c)



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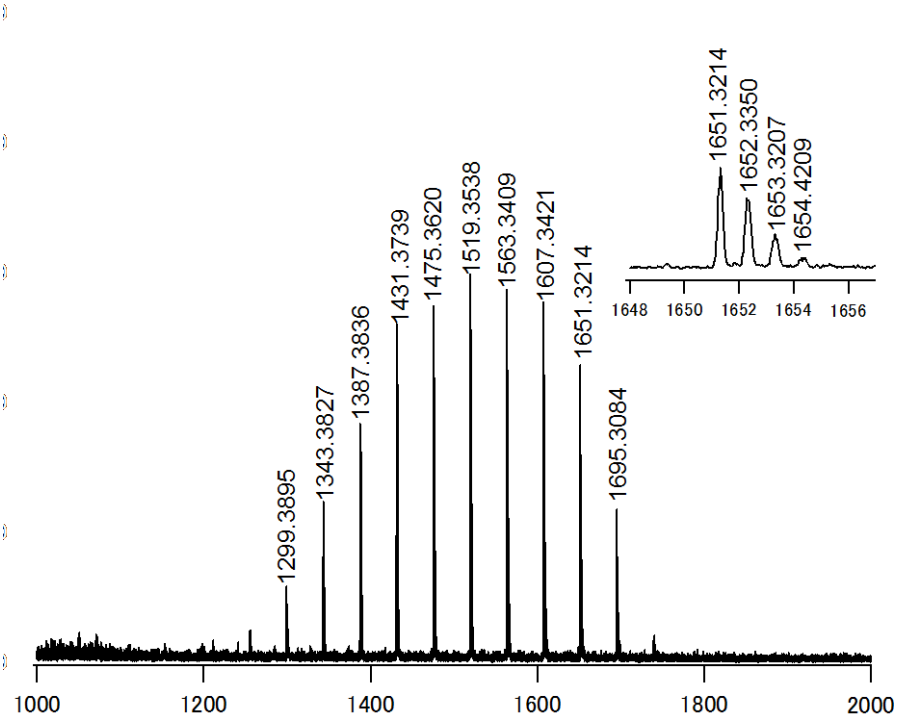
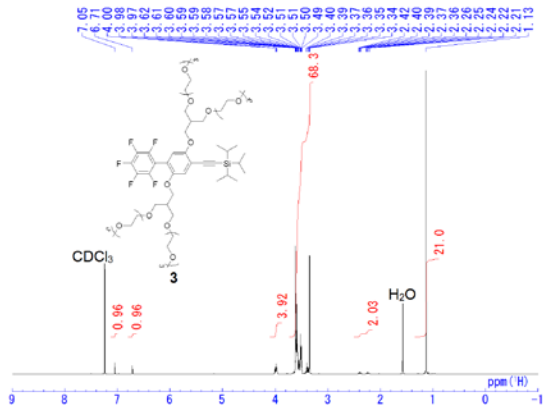


Figure S6. a) ^{1}H, b) ^{13}C, and c) ^{19}F NMR d) MALDI-TOF-MS spectra of **2** ($CDCl_3$).

a)



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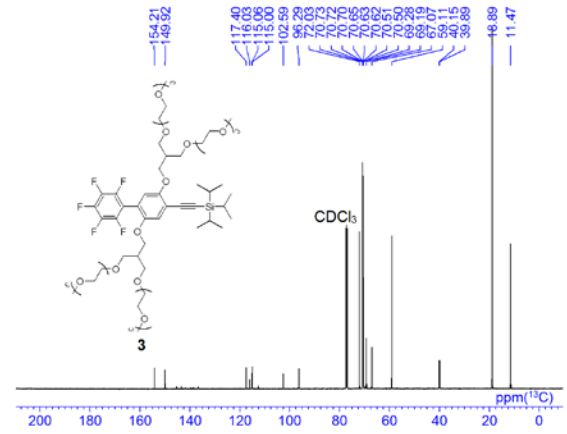

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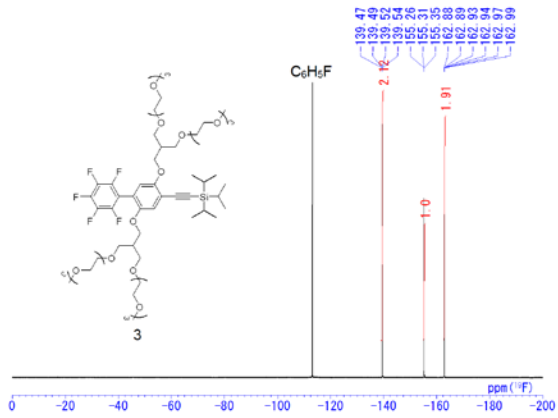
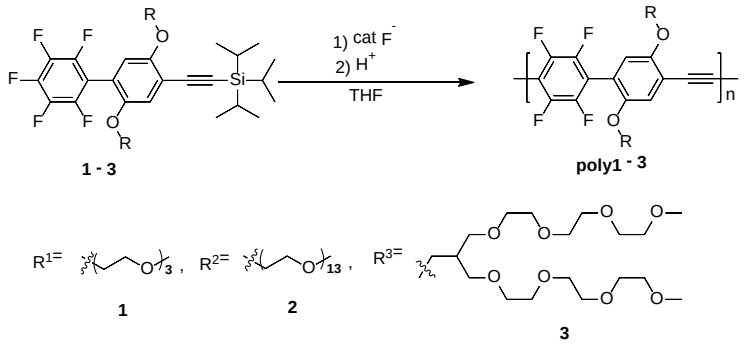


Figure S7. a) ^{1}H, b) ^{13}C, and c) ^{19}F NMR spectra of **3** ($CDCl_3$).

Characterization of polymers

Scheme S2. Polymerization of **1-3**



a) b)

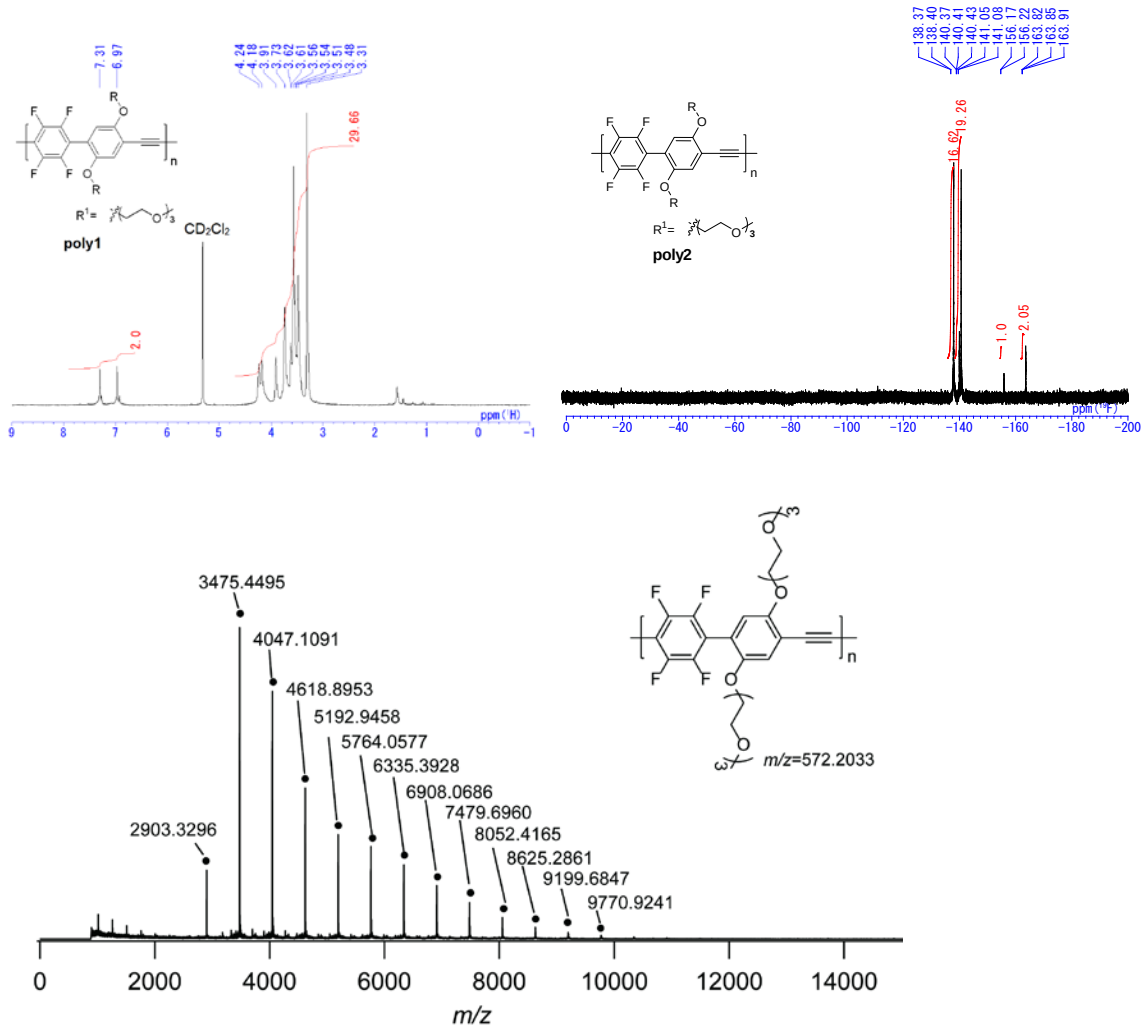
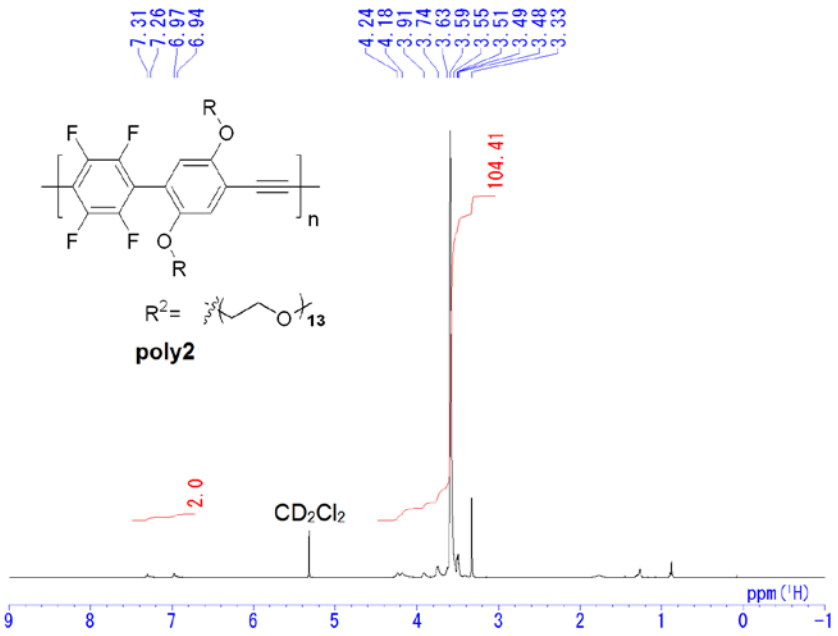


Figure S8. a) ^{1}H, b) ^{19}F NMR (CD_2Cl_2), and c)MALDI-TOF-MS spectra of **poly 1**.

a)



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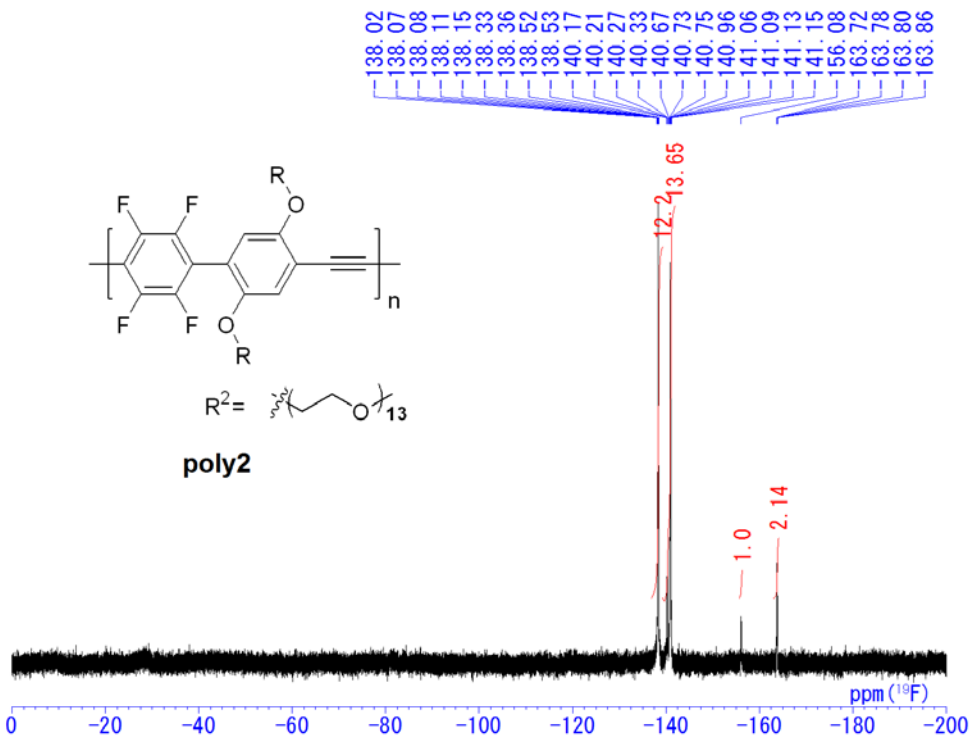

Figure S9. a) ^{1}H and b) ^{19}F NMR spectra of **poly 2** (CD_2Cl_2).

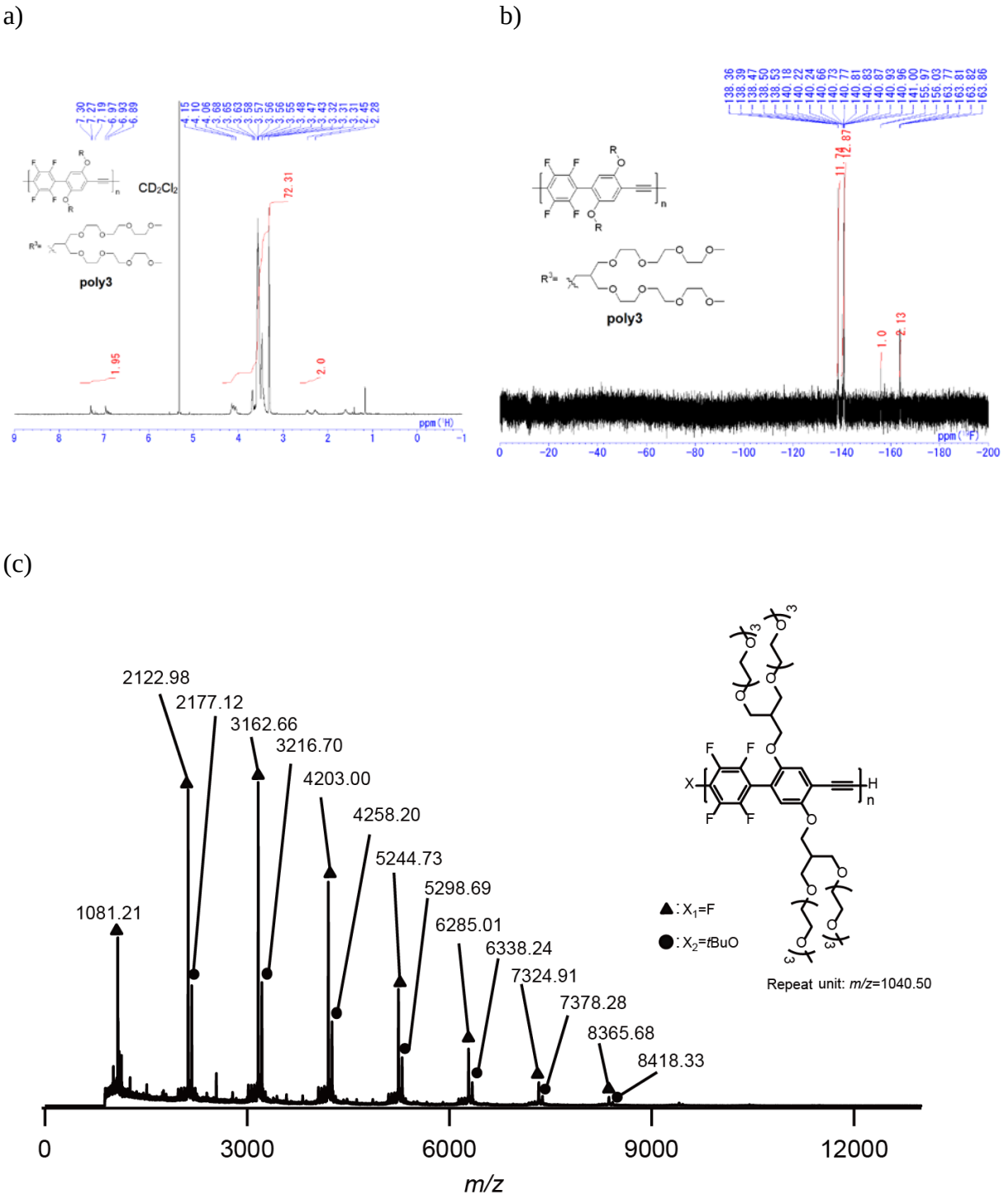

Figure S10. a) ^{1}H, b) ^{19}F NMR (CD_2Cl_2) , and c)MALDI-TOF-MS spectra of **poly 3**.

Polymerization of 2 using TBAF

To study the effect of side chain on the polymerization and obtain the polymer**,** the same method as above was applied to the monomer **2** using TBAF. However, the polymerization didn't proceed well (Figure. 3-3-2-1). Even when polymerization was conducted at 50 ºC in THF and 95 ºC in DMSO, these were almost the same results as run1 in table S1. These results indicate that the large oligo ether groups of the side chains reduce the reactivity of polymerization

Scheme S3. Polymerization of monomer **2** using TBAF.

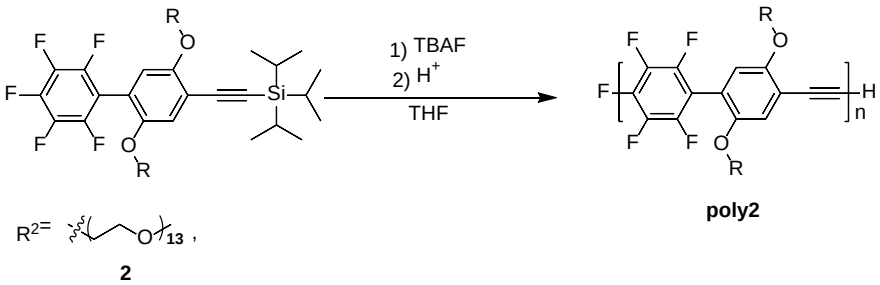

Table S1. Polymerization conditions of monomer **2** using TBAF as the initiator and summary of SEC analysis[a].

Run	Monomer (M)	Initiator (M)	Solvent	T (^{O}C)	Time	[M]/[I]	SEC		
							Mn	Mw	Mw/Mn
1	0.050	0.001	THF	RT	6h	50	2515	3126	1.24
2	0.050	0.001	THF	50	6h	50	2334	2756	1.18
3	0.050	0.001	DMSO	95	6h	50	2059	2262	1.10

[a] Polymerizations were carried out in 2 mL of solvent.

Figure S11. SEC chromatograms for the polymerization of **2** with 2 mol% TBAF in THF (red and blue) and DMSO (black).

Table S2. Polymerization conditions using *t*BuOK as the initiator and summary of SEC analysis[a].

Run	Monomer	Cryptand (M)	Volume (mL)	Time (h)	[M]/[I]	SEC		
						Mn	Mw	Mw/Mn
1	1	0.017	1	24	25	1650	1850	1.1
2		0.033	1			5130	9970	1.9
3		0.066	1			12870	29640	2.3
4		0.250	1			12540	28740	2.3
5	2	0.017	0.5	42	25	5020	5950	1.2
6		0.066	0.5			12100	19005	1.6
7		0.033	0.5			7100	9600	1.3
8		0.250	2			20860	44160	2.1
9		0.500	0.5			20290	43230	2.1
10	3	0.0083	1	24	25	7060	11620	1.6
11		0.017	1			9780	18590	1.9
12		0.033	1			10690	21080	2.0
13		0.25	1			17180	43890	2.6

[a] Polymerizations performed with 0.050 M monomer and 0.002 M *t*BuOK in THF at 50 °C

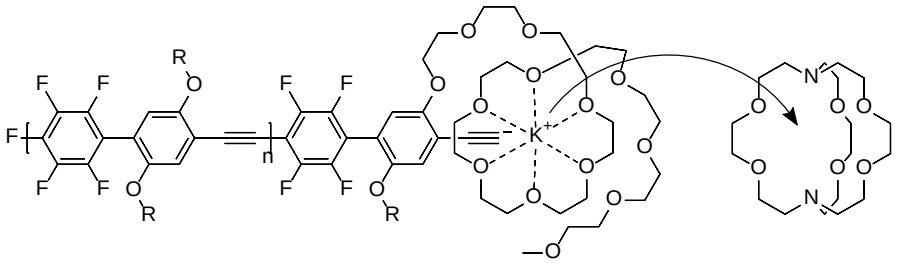

Figure S12. Possible mechanism for enhancing the reactivity of large OE substituted monomers with crypt-222.

Table S3. Solubility of **poly0-4** in various solvents

Polymer	THF	CH_2Cl_2	MeOH	H_2O
poly0	> 5 mM	<1 μM	<1 μM	<1 μM
poly1	> 5 mM	> 5 mM	<1 μM	<1 μM
poly2	> 5 mM	> 5 mM	> 5 mM	0.8 mM[a]
poly3	> 5 mM	> 5 mM	> 5 mM	0.1 mM[a]

[b] measured from dry weight of 5 mL supernatant of saturated solution after centrifugation (10000 g for 15 min)

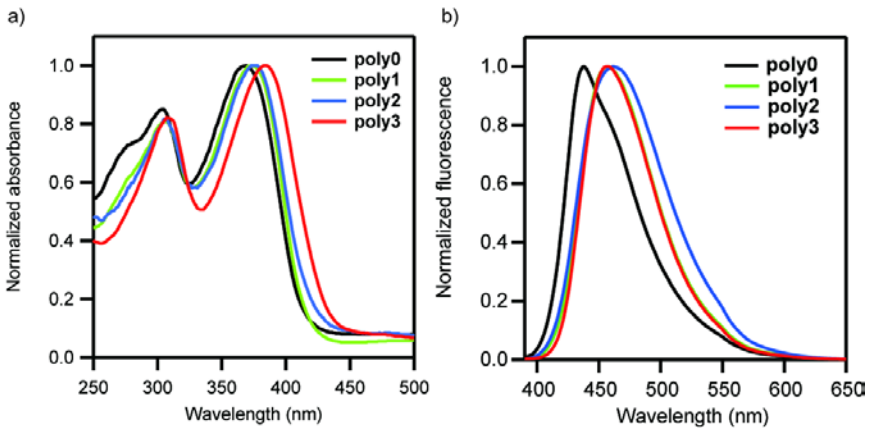

Figure S13. Absorption (left) and emission (right) spectra of **poly0-3** as thin film prepared by spin-casting a 3 wt% toluene solution onto quartz substrate.

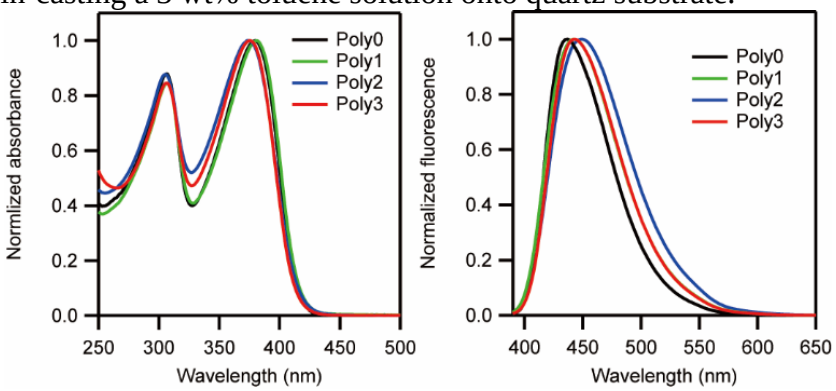

Figure S14. Absorption (left) and emission spectra (right) of **poly0-3** in THF.

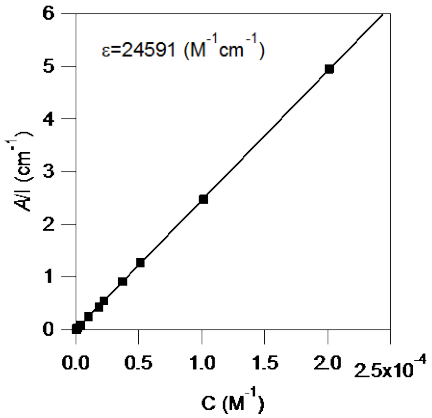

Figure S15. Absorbance at 375 nm ploted against concentration of **poly2** in water.

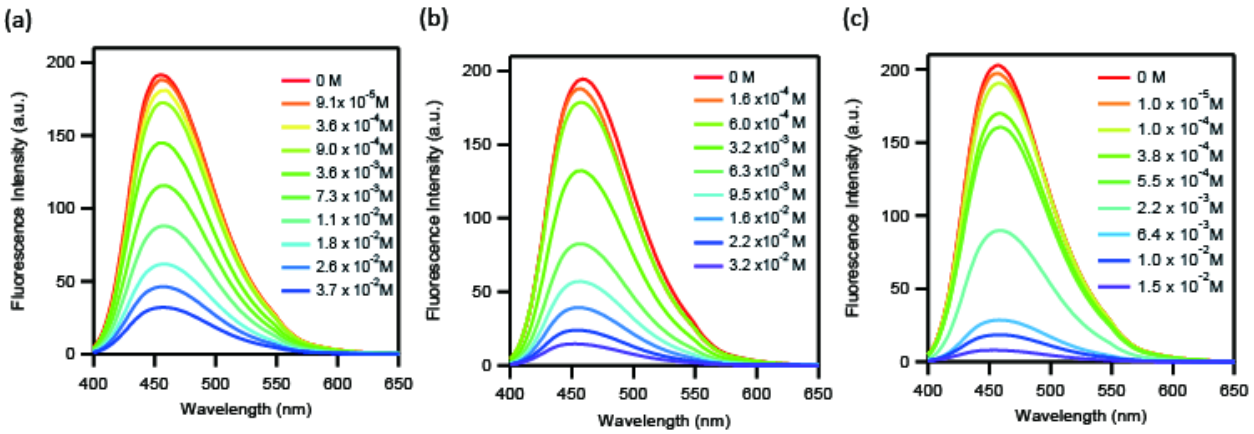

Figure S16. Fluorescence spectra of **poly2** with different concentrations of (a)AN, (b)MA, and (c)TMPD in water. Excitation wavelength is 380 nm.

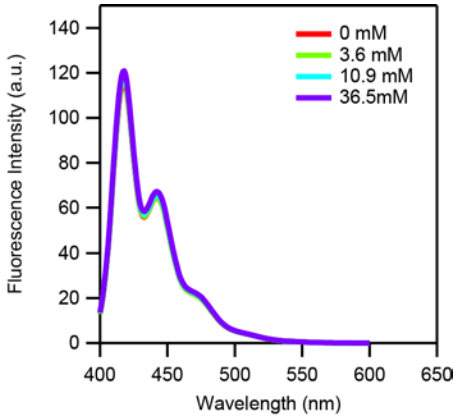

Figure S17. Fluorescence spectra of poly(9,9-dioctyl-9H-fluorene-2,7-diyl) (PFO) upon the addition of AN in THF. Excitation wavelength was 380 nm.

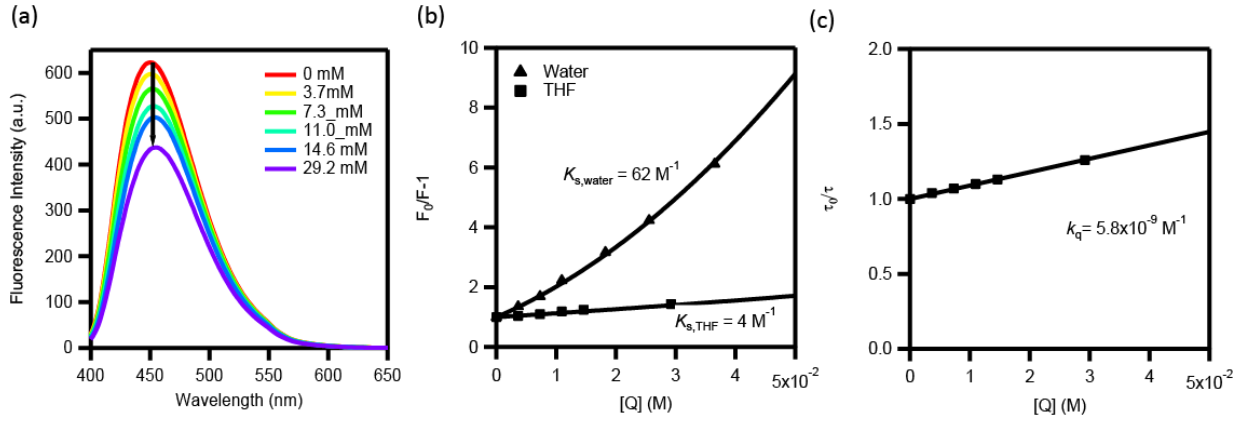

Figure S18. (a) Fluorescence spectra of (b) Stern-Volmer plot of **poly2** at λ_{max} upon the addition of AN in THF. Excitation wavelength was 380 nm.

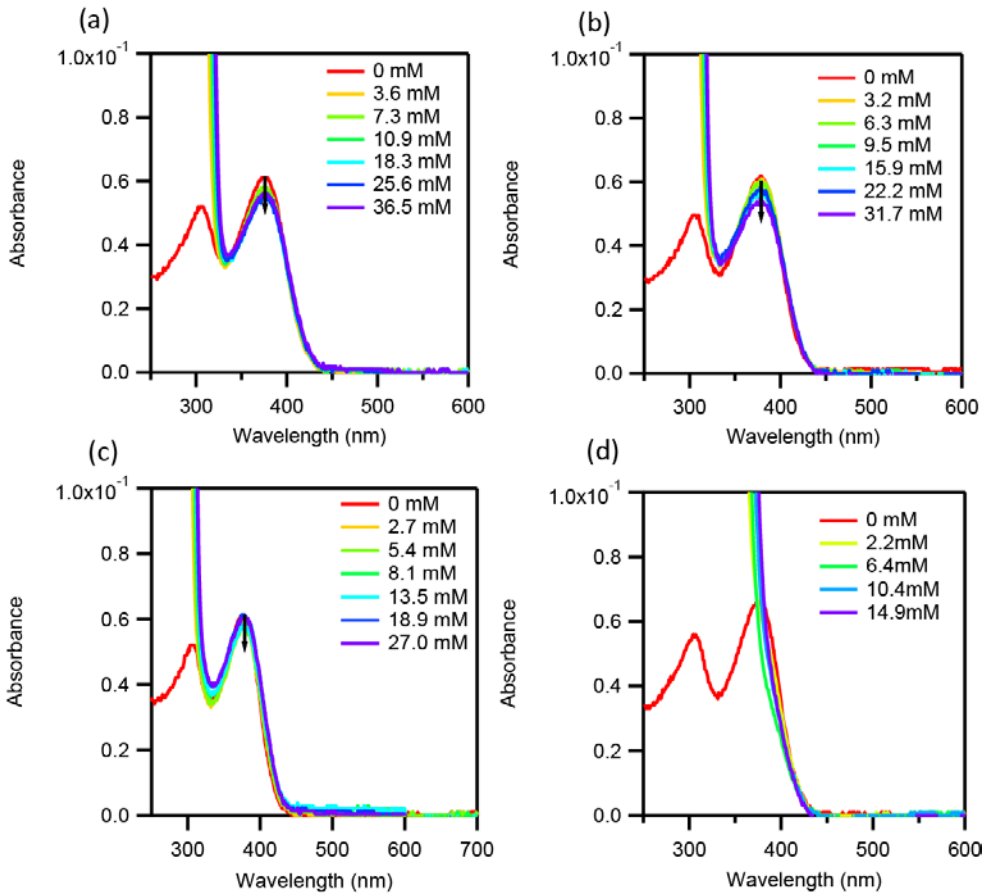

Figure S19. Absorption spectra of **poly2** in water upon the addition of (a)AN, (b)MA, (c)DMA, and (d)TMPD.