New Amorphous Fluoropolymers of Tetrafluoroethylene with Fluorinated and Non-Fluorinated Tricyclononenes. Semiconductor Photoresists for Imaging at 157 and 193 nm.

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Supporting Information

Synthesis of PinAc. Tetramethyloxirane (2,3-dimethyl-2-butene oxide) was prepared by the methyltroxorhenium (MTO) catalyzed epoxidation of 2,3-dimethyl-2-butene with hydrogen peroxide using known methods.[36, 37] A 1 liter flask equipped with a stir bar, and a condenser was charged with methoxyphenol (1.0 g), benzyltrimethylammonium chloride (6.0 g), acrylic acid (88.6 g, 1.23 mole) and 2,3-dimethyl-2-butene oxide (369 g). The mixture was heated to 85 ^{o}C for 17 hours under N_2. Excess epoxide (276 g) was recovered by distillation under reduced pressure at room temperature. The remaining material was dissolved in methylene chloride (400 ml), washed with Na_2CO_3 (aq. 10%), and $NaHCO_3$ (sat., pH = 7-8), then washed with water. The methylene chloride solvent was removed at reduced pressure and the residue was distilled to give 122 g colorless liquid product, bp 37 ^{o}C/0.03 mm to 52 ^{o}C /0.2 mm, 68 % yield based on consumed epoxide. ^{1}H NMR ($CDCl_3$) 1.23 (s, 6H), 1.54 (s, 6H), 3.45 (br s, 1H), 5.80 (dd, J = 10, 1.6 Hz, 1 H), 6.09 (dd, J = 17, 10Hz, 1H), 6.34 (dd, J = 78, 1.6 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$) 21.6, 24.9, 74.6, 89.5, 129.7, 130.3, 166.1 ppm.

Synthesis of 1a. This known compound[38] was prepared by reaction of tetrafluoroethylene (1 equivalent) and norbornadiene (1.25 equivalents) at 180 °C for 8 hr in a sealed metal pressure vessel. The product was purified by spinning band distillation, bp 67 °C at 45 mm.

Synthesis of 1b. A 1-L rocking metal pressure vessel was charged with 120 g of norbornadiene and 0.50 g hydroquinone. The vessel was closed, cooled in dry ice,

evacuated and charged with 347 g of perfluoropropylvinyl ether. The vessel was heated to 190 °C for 24 hr while the internal pressure decreased from a maximum of 267 psi to 36 psi. The vessel was cooled to room temperature and vented. The vessel contents were distilled though a Vigreux column giving 341 g of product, bp 142-146 °C at 200 mm. ^{1}H NMR (δ, $CDCl_3$) 1.2 - 1.9 (m, 2H), 2.55 (m, 2H), 3.22 (m, 2H), 6.18 (s, 2H); ^{19}F NMR (δ, $CDCl_3$) -80.7 (1F), -81.9 (3F), -86.3 (1F), -107.8 (0.48 F), -111.3 (0.52 F), -120.6 (0.52 F), -122.4 (0.48 F), -126.0 (0.52 F), -130.0 (2F), -136.0 (0.48 F). The fluorine NMR indicates a mixture of isomers in an approximately 52:48 ratio.

Synthesis of 1c. A 400 mL Hastelloy shaker tube was charged with norbornadiene (115 g, 1.25 mol), BHT (0.4 g), and ethyl pentafluoroisopropenyl ether[39] (100 g, 0.62 mol). The vessel was chilled, evacuated, and then heated at 175°C for 24 hr. The cooled mixture was fractionated by distillation at reduced pressure. There was obtained 95.8 g of colorless liquid, bp 77°C – 84°C (8.8 mm). Product consisted of a mixture of stereoisomers, comprising an 80/20 *exo/endo* (4-membered ring junction) distribution and a ca. 60/40 distribution arising from -CF_3 and –OC_2H_5 group orientations. ^{19}F NMR (C_6D_6) showed signal assigned to *exo* product exhibiting 2 AB patterns, low-field branches at –100.55 (ddq, J= 218, 5.4, 13.7) and –102.17 (ddd, J= 215, 14.7, 7) and high-field branches at –118.15 (d, J=218) and –119.60 (d of m's, J=214, 7.6), and CF_3 signals at –67.88 (d, J=7.1) and –73.2 (J=14.2). A pair of minor isomer signals was also evident: 2 AB patterns, low-field branches at –99.6 (ddq, J=240, 8.2, 17.4) and –101.8 (dd, J=237, 8.7), and high-field branches at –105.2 (dq, J= 237, 15.8) and –106.3 (d, J=233), one of the CF_3 doublets appeared at –69.3 (J=18, a= 0.39), the other was obscured. GC/MS revealed two major and two minor isomers, each exhibiting M+ with m/e = 268.

Synthesis of 1d. A 400 ml Hastelloy shaker tube was charged with 35 g of quadricyclane (0.3 mol calculated for 80% purity quadricyclane, sample contained 15 % ether and 5 % norbornadiene) and 50 g (0.3 mol) of 3,3,3-trifluoro-2-(trifluoromethyl)propene (DuPont) and kept at 120 °C for 16 hr. The reactor was vented, unloaded and crude product (58 g) was distilled under vacuum to give 41 g of **1d**; bp 72-

73 °C at 44 mm. ^{19}F NMR (δ, $CDCl_3$): -66.18 (3F, q; 10.3Hz), -74.30 (3F, q; 10.3Hz); ^{1}H NMR: 1.40 (1H), 1.8-2.4 (5H, m), 2.87 (1H), 3.07 (1H), 6.03 (1H, m), 6.13 (1H, m). Anal. Calcd: C, 51.57%; H, 3.93%; F, 44.49%. Found: C, 51.29%; H, 3.88%; F, 43.86%.

Synthesis of 1e. a). Preparation of 2-fluoroacroyl fluoride (CH_2=CFC(O)F). Into a 3L flask equipped with a mechanical stirrer, dry-ice condenser and thermocouple was placed dry DMF (1.3 L), hydroquinone (6 g), and zinc (130 g). Sodium iodide (160 g) was added to the flask under N_2 flow with stirring in one portion. The reaction mixture was stirred at RT for 15 min (the internal temperature increased to 29 °C). Tetrafluorooxetane[40] (130 g) was added dropwise to the reaction mixture, starting at a temperature of 35 °C. The addition was complete in 1 hr. The internal temperature was kept between 36 and 42 °C most of time, but increased to 47 °C at the end of the reaction for about 5 min. The mixture was stirred at 35 – 25 °C for 3 hr after the addition. The product was distilled at reduced pressure (~5 mm) and collected in a dry-ice trap and a liquid N_2 trap in series. A total of 79.5 g of liquid was obtained, which contained about 65% of product, 30% DMF and 5% impurities, based on NMR analysis. Calculated yield was 52%.

b) Preparation of cycloadduct of quadricyclane and CH_2=CFC(O) F. A 400 ml metal pressure vessel was charged with cold solution of 79 g of CH_2=CFC(O)F, (which contained 30% of DMF and 0.6 g of hydroquinone) in 100 ml of dry ether, and 65 g of cold quadricyclane (90% purity, 10% of norbornadiene and MeO-t-Bu) was added. The reactor was kept at 110 °C for 16 hr. The solvent and volatiles were removed from crude product under vacuum to give 111 g of crude cycloadduct of 70% purity. The rest was DMF (~ 15%) and others (15%). There are two isomers: ^{19}F NMR -26.3 (d, J = 26 Hz, 1F), -150.7 (quintet, J = 26 Hz, 1F); other isomer -20.2 (d, J = 20 Hz, 1F), -171.2 (qq, J = 19, 7 Hz, 1F) ppm. The crude product was used for the next step of the reaction without further purification.

c) Preparation of **1e**. A 500 ml flask, equipped with dry-ice condenser, thermocouple, addition funnel and magnetic stirrer, was charged with dried CsF (15 g,

0.1 mol) and CH_3CN (150 ml) in a dry box. The solution of 111 g of the above crude cycloadduct (about 0.42 mol) in CH_3CN (50 ml) was added over a 5 min period. The reaction mixture was stirred at ambient temperature for 15 min, then cooled to 5 °C. Trifluoromethyltrimethylsilane (120 g, 0.85 mol) was added slowly over 1 hr and 40 min. The resulting mixture was warmed to 25 °C over 2 hr and agitated at 25 °C for 16 hr. The liquid was decanted, and the solid was washed with 50 ml of dry CH_3CN. The combined organic fractions were added to 500 ml of 5% hydrochloric acid. The resulting mixture was stirred at RT for 45 min. The mixture was extracted with CH_2Cl_2 (3 X 200 ml). The combined extracts were washed with HCl (5%, 4 X 150 ml), and dried over $MgSO_4$. The solvent was removed on a rotary evaporator to leave 155 g of crude product, which was distilled under vacuum to give fraction 1, 5 g (bp < 42 °C at 0.05 mm) and fraction 2, 101.7g, bp 51-63 °C at 0.05mm (mainly 61-62 °C/0.05 mm. Both fraction 1 and fraction 2 contained the trimethylsilyl ether of **1e**. They were treated with Bu_4NF (80 g) in THF (200 ml) at RT overnight. HCl (5%, 300 ml) was added and the organic layer was isolated. The aqueous layer was extracted with ether (2 X 200 ml). The ether extracts were combined with the organic layer and washed with water (3 X 100 ml), dried over Na_2SO_4, and concentrated to give a liquid. Distillation of the liquid gave **1e**, 77g, bp 50 - 55 °C at 0.05mm. Overall yield (from oxetane to the alcohol) was 25%. The product was a mixture of the two isomers in a 1:1 ratio. ^{19}F NMR -72.5 (dm, J = 147 Hz, 6F), -171.8 (m, 1F); other isomer –73.8 (dm, J = 363 Hz, 1F), -145.6 (m, 1F) ppm.

Synthesis of 1f. a) Preparation of $CH_2=C(CF_3)C(O)Cl$. To 45 g of phthaloyl dichloride in a round-bottom flask, equipped with distillation head, was added 28 g of $CH_2=C(CF_3)C(O)OH$. The reaction mixture was heated to 150 °C with simultaneous distillation of the product, which was collected [28 g (88%) of fraction 86, 100 °C], and used in the next step without further purification.

b) Reaction of $CH_2=C(CF_3)C(O)Cl$ with quadricyclane. To the solution of 22 g of quadricyclane in 100 ml of dry ether, 28 g of $CH_2=C(CF_3)C(O)Cl$ was added at 10 - 20 °C. (The reaction is exothermic!). The reaction mixture was kept at 25 - 35 °C for 12 hr. The solvent was removed under vacuum and the residue was distilled to give 36 g

(71%) of cycloadduct**,** bp 103 - 108 °C at 15 mm. Mixture of two isomers, ratio 60:40. ^{19}F NMR ($CDCl_3$), major: –66.53 (s) ppm; minor: -74.75 (s) ppm.

c) Preparation of **1f**. To the mixture of 65 g of dry CsF and 100 ml of dry acetonitrile in a 1 L flask equipped with thermometer, addition funnel and dry-ice condenser was slowly added the solution of the above product in 200 ml of dry CH_3CN. The reaction mixture was agitated 1 hr at ambient temperature and cooled to 10 °C. Trifluoromethyltrimethylsilane (110 g) was added slowly at 10 -15 °C. The reaction mixture was brought to ambient temperature and agitated for 14 hr. 400 ml of 10% hydrochloric acid was slowly added to the reaction mixture at 15 - 20 °C (pH<1). The reaction mixture was extracted with CH_2Cl_2 (3 x 100 ml), the combined organic layers were dried over $MgSO_4$ and then the solvent was removed under vacuum. The residue was distilled under reduced pressure to give 30 g (24%) of fraction bp 74 - 75 °C at 0.75 mm of **1f**. According to NMR data, the product was a mixture of two isomers in the ratio of 60:40. ^{19}F NMR ($CDCl_3$) major: -61.27 (3F, m), -68.73 (3F, m), -71.21 (3F, m); minor: -70.55 (3F,m), -71.35 (3F,m), -72.56 (3F,m). Anal. Calc. for $C_{13}H_{11}F_9O$: C, 44.08; H, 3.13; F, 48.27. Found: C, 43.80; H, 3.20, F, 48.48.

Synthesis of 1g. a) Preparation of cycloadduct of quadricyclane and CF_2=CFC(O)F. A Fischer/Porter glass pressure vessel was charged with quadricyclane (15.1 g, 163 mmol) and a stirring bar. The liquid was cooled to –78°C and the vessel was evacuated. Trifluoroacryloyl fluoride (19 g, 150 mmol) was condensed in a gas trap and transferred under vacuum to the vessel. The stirred contents were allowed to warm slowly and then maintained at 45°C for 24 hr. The mixture was cooled to room temperature and a small volume of low-boiling material was transferred from the reactor to a trap under vacuum. The remaining reaction mass was characterized the cycloadduct in purity estimated as >95% based on NMR analysis. ^{19}F (C_6D_6) +36.35 (a =59.3, COF), +29.22 (a=33.9, COF), low-field portions of AB patterns at –100.15 (a=36.8) and –105.35 (a=64.2), up-field portions of AB patterns at –118.6 (major) and –119.25 (minor), CF at –165.87 (a=50.9) and –188.0 (a=31.1).

b) Preparation of **1g**. To the mixture of 35 g of dry CsF and 200 ml of dry THF in a 500-ml flask equipped with thermometer, addition funnel and dry-ice condenser was slowly added the solution of the above cycloadduct in 50 ml of dry THF and 49 g of trifluoromethyltrimethylsilane at 10-15 °C. The reaction mixture was brought to ambient temperature and agitated for 14 hr. 500 ml of 10% hydrochloric acid was slowly added to the reaction mixture at 15 - 20 °C (pH<1). The reaction mixture was extracted with CH_2Cl_2 (3 x 100 ml), the combined organic layers were washed twice with 10% HCl, dried over $MgSO_4$ and the solvent was removed under vacuum. The residue was distilled to give 32 g (60%) of fraction b.p. 46 - 48 °C at 0.05 mm of **1g**. According to NMR data, the product was a mixture of two isomers in the ratio of 65:35. ^{19}F NMR ($CDCl_3$,) major: -73.38(3F, m), -73.90(3F, m), -102.82(1F, dm; 217 Hz); -120.87(1F, dqd; 217; 16.4; 6.6 Hz)), -160.58(1F,m); minor: -71.70 (3F,m), -72.56(3F,m), -106.03 (1F, dm; 225.5 Hz), -117.53(1F, dd; 225.5; 9.8Hz). Anal. Calc. for $C_{12}H_9F_9O$: C, 42.37; H, 2.67. Found: C, 41.43; H, 2.70.

Synthesis of 1h. A Fisher/Porter glass pressure vessel was charged with quadricyclane (18.0 g, 195 mmol) and 1,1, 3,3,3-pentafluoro-2-propenyl benzoate (32.86

g, 130.3 mmol). The sealed vessel was heated at 125 °C for 144 hr. The reaction mixture was cooled, and residual C_7H_8 was removed under reduced pressure. Kugelrohr distillation provided 13.5 g of lower-boiling liquid, bp 23 – 60 °C at 0.05 mm (41% of initial charge of 1,1, 3,3,3-pentafluoro-2-propenyl benzoate) and 27.3 g of colorless oil, bp 92 – 97 °C at 0.03mm (60.9% of theory). ^{19}F NMR (C_6D_6) showed: –67.93 (d, J=11.4, a= 0.12), -72.98 (dd, J=16.9, 1.6, a= 0.13), two AB patterns: -99.0 (J= 214.7, and doublet couplings of 6.0 Hz, 14.7 Hz, a= 0.042), –118.81 (J= 215, several other couplings, a=0.041), and –101.6 (J=222, along with doublet of quartets, J= 6.0, 17.4, a= 0.044), -114.82 (J=221, other couplings not resolved, a= 0.046). ^{1}H NMR (C_6D_6): 8.10 and 8.02 (m's, a= 2.00, ortho H's), 7.06 (m) and 7.00 to 6.92 (m, combined a = 3.12), 2 sets of vinyl signals 5.73, 5.68, and 5.62 – 5.56 (a=2.03), 3.16 and 3.14 (overlapping bd singlets, a= 1.00, bridgehead), 2.75 (bd s, overlapping m, a= 0.95), 2.66 (bd s, a=0.52), 2.58 – 2.47 (overlapping m's, a=1.02), 2.27 (m, a= 0.54), 2 sets of CH_2 AB patterns, 2.09, 1.15 (d, J= 10.1Hz), and 1.72, 1.00 (d, J= 9.7 Hz).

The distilled cycloadduct (27.3 g, 79.1 mmol) was added to a solution of potassium hydroxide (13.35 g, 203 mmol) in methanol (250 mL) and water (167 mL). The mixture was stirred rapidly at room temperature for 4.5 hr. Most of the methanol was removed under reduced pressure. Water (150 mL) was added and the pH was adjusted to ca. 7.0 by addition of hydrochloric acid. Product was extracted with methylene chloride (3 x 150 mL) and the extract was dried and stripped to give 20.7 g almost colorless oil. Kugelrohr distillation gave 19.6 g (ca. 100%) of colorless oil, bp 35° – 38 °C at 0.05 mm. ^{19}F NMR (C_6D_6): -74.02 (d, J= 7.1 Hz, a=2.77), -79.25 (dd, J= 2.0, 14.7), two sets of AB patterns, -103.05 (ddd, J= 6.5, 13.7, 213, a=0.93), -105.34 (dddq, J = 218, 15, 5.4, 15, a=1.02), -119.19 (d, J=217.5, a=1.01), -123.07 (d of m's, J = 213, a= 0.93). ^{1}H NMR (C_6D_6): 5.67 (dd, J=3.3, 5.8) and 5.54 (J=3.3, 5.8, vinyl signals for isomer A), 5.62 (2nd order AB pattern, combined vinyl signal area = 2.00), 2.80 (bd s, a= 0.49) 2.69 (m) and 2.67 (s, combined a= 1.51), 2.46 (bd s, a=0.50), 2.28 (m, a= 0.50), 2.16 (m, a= 0.55), 2.02 to 1.96 (overlapping m, a= 1.02), 1.93 (bd s, a= 0.51), 1.81 (d, J = 10, a = 0.53), 1.71 (overlapping d's, J ca. 7.2, a=0.48), 1.11 (d, J ca. 10) and 1.08 (d, J ca. 10, combined a=1.02).

Synthesis of 1i. This monomer was prepared as described elsewhere.[11]

Synthesis of 1j. A 400 mL Hastelloy C276 reaction vessel was charged with 2,5-norbornadiene (Aldrich, 98%, 100 g) and hydroquinone (0.5 g). The vessel was cooled to -1 ^{o}C, evacuated to 250 Torr, and purged with nitrogen. It was evacuated again and 2-(1,2,2-trifluorovinyloxy)-1,1,2,2-tetrafluoroethanesulfonyl fluoride (305 g) was added. The reactor temperature was increased to 190 ^{o}C and held there for 6 hr. After cooling, the crude product was purified by vacuum distillation to give **1j** as a colorless liquid (361 g, 89% yield, mixture of two isomers, ratio ~1:1); bp 110 ^{o}C at 40 mm. MS: m/e 372 (M^+), 189 ($C_9H_8F_3O^+$), 173 ($C_9H_8F_3^+$), 141 ($C_8H_7F_2^+$), 115 ($C_6H_5F_2^+$), 91 ($C_7H_7^+$), 77 ($C_6H_5^+$), 66 (base, $C_6H_5^+$), 51($C_4H_3^+$).

Synthesis of 1k. A 400 ml Hastelloy shaker tube was charged with 50 g (0.54 mol) of 2,5-norbornadiene (Arcos, 96%), 100 g (0.22 mol) of CF_2=$CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$ (DuPont), 0.5 of hydroquinone and kept at 200 °C for 20 hr. The reaction mixtures of three consecutive runs were combined and distilled was distilled under vacuum to give 309 g (85%) of **1k** (mixture of two isomers, ratio~ 1:1); bp 88-92 °C at 0.27 mm Calc. for $C_{14}H_8F_{14}O_4S$, C, 31.24; H, 1.50; F,49.41. Found: C, 30.85; H 1.51; F, 49.30%.

Synthesis of 1l. A Fischer/Porter glass pressure vessel was charged with quadricyclane (15.1 g, 163 mmol) and a stirring bar. The liquid was cooled to –78 °C and the vessel was evacuated. Trifluoroacryloyl fluoride (19 g, 150 mmol) was condensed in a gas trap and transferred under vacuum to the vessel. The stirred contents were allowed to warm slowly. The mixture was heated at 45 °C for 36 hr. The mixture was cooled to room temperature and a small volume of low-boiling material was transferred to a trap under vacuum. Crude adduct acid fluoride was treated with ether (70 mL) and added by canula to a 3-neck flask (under N_2) fitted with thermo-well, stir bar, and addition port. The solution was cooled to –20 °C and treated portion-wise with a solution of potassium t-butoxide (17.7 g, 150 mmol) in ether (130 mL)/THF (40 mL), keeping the reaction temperature at –15 °C during addition (40 min). The mixture was

allowed to warm slowly to room temperature. The reaction mixture was cooled in ice, and then added to a mixture of ether (400 mL) and ice water (400 mL). The pH of aqueous phase was ca. 8; the organic layer was washed with brine, and dried (Na_2SO_4, $MgSO_4$), and stripped. Kugelrohr distillation gave 35.6 g (87%) of colorless oil, bp 50 – 65 °C. To ensure that the monomer sample was free of higher-boiling residue, it was re-distilled to give 35.0 g of material. ^{1}H NMR (C_6D_6): 5.73 – 5.62 (m, a= 2.00), 3.35 (bd s, a=0.64), 2.81 – 2.72 (overlapping m, a= 1.72), 2.42 – 2.28 (m, a=1.01), 2.12 – 2.06 (m) and 2.50 – 1.99 (overlapping m, a=1.03), 1.69 (d, down-field portion of AB pattern, J=9.8 Hz, a=0.63), 1.34 (s, a= 3.55, $OC(CH_3)_3$, minor isomer), 1.28 (s, $OC(CH_3)_3$, major isomer) and 1.25 (d, up-field portion of AB pattern, major isomer, combined a= 6.92), 1.15 (d, up-field portion of AB pattern, minor isomer, a = 0.40). ^{19}F NMR (C_6D_6) showed 2 AB patterns, -101.86 (ddd, J=5.4,14.2, 216, a=35.5, minor isomer), -107.05 (dddd, J=2.7, 6.0, 16.3, 218, a=62.9, major isomer), up-field branches at –119.00 (J= 2.7, 217, a=63.3), -120.8 (d of m's, J= 3.8, 216, a=36.3), -160.67 (d of m's J= 2.2, 26.7, a=59.9), -186.76 (m, a=34.1). Spectra were consistent with a ca. 63/37 mixture of stereoisomeric adducts. GC/MS showed two components, 2/1 ratio, which exhibited very similar fragmentation patterns and showed M^+ with m/e=274 and M-CH_3 ions consistent with the desired t-butyl esters.

Synthesis of 1m. A mixture of 30 g CH_2=CFC(O)F (containing 35% DMF) (0.22 mol) and 35 ml of quadricyclane in 100 ml of dry ether was kept at 100 °C for 16 h. Crude reaction mixture was fractionated to give 25 g (80% purity, 52% yield) of fraction b.p. 57 - 82 °C at 20 mm. This material was dissolved in 50 ml of dry DMF, cooled to –20 °C and a solution of 13 g of dry potassium t-butoxide in 100 ml of dry DMF was slowly added at a rate keeping the internal temperature at –20 to –15 °C. The reaction mixture was warmed to room temperature and agitated overnight. The reaction mixture was diluted with 500 ml of water and extracted with CH_2Cl_2 (1 x 100 ml and 1 x 50 ml). The combined organic layers were washed with a solution of 50 ml of hydrochloric acid in 500 ml of water (3 x 150 ml) and dried over $MgSO_4$. The solvent was removed under vacuum and the residue was distilled to give 8.9 g of fraction bp 85 - 94 °C at 0.55 mm

(80% purity **1m**), the remainder DMF) and 11.5 g of **1m** as a mixture of two isomers (ratio 3:1); bp 94 - 96 °C/0.55 mm. Calculated yield 71.4%. ^{19}F NMR: -145.16 (m) major; -170.54 (m) minor.

Synthesis of 1n. To the solution of 75 g (0.3 mol) of adduct of quadricyclane and CH_2=C(CF_3)C(O)Cl (see preparation of **1f**) in 100 ml of dry THF placed in 1 L flask equipped with thermometer, addition funnel and water condenser was slowly added the solution 36 g (0.32 mol) of KOC(CH_3)$_3$ in 150 ml of dry THF at 0°C. The reaction mixture was warmed up to ambient temperature (~2 hr) and agitated for 2 hr at ambient temperature. Solvent was removed under vacuum, residue was filtered and distilled under reduced pressure to give 52 g (60%) of **1n**, bp 72-77 at 1.9 mm as a mixture of two isomers, ratio 53:47. ^{19}F NMR ($CDCl_3$), major: -74.75 (s) ppm; minor –66.53 (s) ppm.

Synthesis of 1o. This known compound was prepared by heating a mixture of 100 ml of t-Bu-acrylate with 88 g of quadricyclane at 90 °C for 96 h. Distillation of crude product (159 g) afforded 27 g (14%), bp 125-130 at 18 mm.

Synthesis of 1p. A mixture of 55 g of CH_2=C[C(O)OC(CH_3)$_3$]C(CF_3)$_2$)OH[32, 33] and 25 g of quadricyclane was heated with agitation at 100-110 ^{o}C for 10 hr. The reaction mixture was distilled under vacuum (short-path distillation) to give 45 g (65%) of **1p**, as white solid, mp 118 - 120 ^{o}C, (mixture of two isomers, ratio 97:3). ^{1}H NMR (acetone-d_6, major isomer): δ 1.2 (1H,d), 1.5 (9H,s), 1.6 (1H,s), 1.9 (1H,m), 2.1 (1H,d), 2.6 (2H,m), 2.8 (2H), 3.0(1H), 6.0(2H,m). ^{19}F NMR (major): δ -69.8 (3F, q), -71.60 (3F,q); minor –70.0 (3F,q), -73.8 (3F, q). Anal. Calc. for $C_{17}H_{20}F_6O_3$: C, 52.85; H, 5.22 %. Found: C, 53.04; H, 4.98%.

Synthesis of 1q.[41] a) Synthesis of Di-*tert*-butyl Fumarate.[42] Procedure was slightly modified from literature procedure. To a 1 L three-neck round-bottom flask equipped with a stir bar, thermometer, addition funnel, reflux condenser, and nitrogen inlet were added potassium *tert*-butoxide (110.0 g, 0.981 mol) and dry *tert*-butyl alcohol

(500 mL). To this mixture was added, dropwise, fumaryl chloride (75.0 g, 0.490 mol). During the addition an exothermic reaction started and further addition was continued at such a rate as to keep the reaction temperature at 50°C. The black solution was heated to reflux for 4 hr. After this time, the solution was cooled to room temperature, poured into water (1 L), and the water layer was extracted with diethyl ether (4 x 200 mL). The combined extracts were dried with magnesium sulfate, filtered, and evaporated. The black crude oil was vacuum transferred (80-100°C / 0.05 torr) using a short-path distillation head (water in the condenser was kept at 70°C to keep product from crystallizing inside the condenser). After cooling, a white crystalline solid was obtained (mp ~67-70°C, 60.0 g, 54%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.46 (18H, s, CH_3), 6.63 (2H, s, CH=CH). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 28.0, 81.6, 134.5, 164.4.
b)Synthesis of **1q**. To a 500 mL round-bottom flask equipped with a stir bar, thermometer, reflux condenser, and nitrogen inlet were added di-*tert*-butyl fumarate (82.0 g, 0.359 mol) and quadricyclane (60.0 g, 0.651 mol, Exciton Inc.). The mixture was heated at 110°C for 18 h. The resulting crude product was distilled under vacuum (short-path distillation) to yield a white solid (80 g, 81%) which crystallized upon standing. ^{1}H-NMR (ppm, $CDCl_3$): δ 1.20 (1H, d), 1.35 (18H, d), 1.43 (1H, m), 1.92 (1H, t), 2.15 (1H, dd), 2.63 (1H, dd), 2.75 (1H, s), 2.90 (1H, s), 3.40 (1H, dd), 5.92 (2H, m).

Synthesis of 1r. a)Synthesis of Di-*tert*-butyl Maleate. A 400 mL pressure vessel was swept with nitrogen and charged with diethyl ether (100 mL), concentrated sulfuric acid (5 mL), and maleic acid (50.0 g, 431 mmol). The vessel was closed, cooled in dry ice, evacuated, and charged with isobutene (100 g, 1.78 mol). The vessel contents were warmed to room temperature and agitated for 18 hr. The vessel was vented to one atmosphere and the contents were poured into a beaker containing water (250 mL), ice (250 g), and sodium hydroxide (70 g). The mixture was stirred at room temperature for 1 h to evaporate excess isobutene. The organic layer was separated in a separatory funnel, and the aqueous layer was extracted with diethyl ether (3 x 200 mL). The combined organic extracts were dried with magnesium sulfate, filtered, and evaporated to yield a white solid (77.0 g, 78%). No further purification was necessary. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.48 (18H, s, CH_3), 6.03 (2H, s, CH=CH).

b) A mixture of 46 g of *tert*-butyl maleate and 25 g of quadricyclane (Exciton Inc., USA, 99%) was refluxed (120-125°C) for 120 hr. Crude product was distilled under vacuum (short path distillation) to give 80g (81%) of **1r**, bp 126 °C at .03 mm which crystallized on standing. ^{1}H NMR ($CDCl_3$): δ 1.2 (1H, d), 1.4 (18H, d), 1.6 (1H, d), 2.1(1H, m), 2.6(1H, d), 2.7(1H, m), 6.0 (2H,m).

Synthesis of 2a-c. These monomers were prepared as described.[28]

Synthesis of 2d. To a solution of sodium hypochlorite, prepared by addition of 56 g of chlorine gas to the solution of 100 mL of 50% NaOH in 200 mL of deionized water at –5 to 0 ^{o}C, was added 1 g of $(C_4H_9)_4N^+HSO_4^-$ followed by slow addition of the solution of **2c** in 150 mL of ether at 5-10°C. The reaction mixture was allowed to warm to room temperature and was agitated overnight (total reaction time 16 hr). The organic layer was separated and the water layer was extracted with ether (100 mLx1). The combined organic solutions were dried over $MgSO_4$ and concentrated under reduced pressure. The residue (58 g) was distilled to give 50 g (94%) of **2d** (99% purity), bp 31-32C/ 0.1 mm. According NMR crude reaction mixture contained only one isomer of **2f**, however, in distilled material the second isomer (~5%) was present. ^{19}F($CDCl_3$), major isomer: -68.30 (3F, q, J=7.5 Hz), -70.84 (3F, q, J=7.5 Hz); minor isomer: -68.71 (3F, q, J=6.9 Hz), -71.15 (3F, q, J=6.9 Hz) ppm. ^{1}H($CDCl_3$), major isomer: 1.80(1H,d. quint., J=10.2, 1,5 Hz), 2.02(1H,d, J=10.2Hz), 2.98 (1H, m), 3.10 (1H, d, J=5.1 Hz), 3.26 (1H, m), 4.71 (1H, dt, J=5.1, 1.2 Hz), 6.04(1H, dd, J= 5.8, 3.1 Hz), 6.30 (1H, dd, J= 5.8, 3.1 Hz); minor isomer: 1.76 (1H,d. quint., J=10.1, 1.5 Hz), 2.25(1H,d, J=10.1Hz), 3.03 (1H,m), 3.18 (1H, m), 3.24 (1H, m), 4.51 (1H, dt, J=5.0, 1.5 Hz), 6.01(1H, dd, J= 5.5, 3.1 Hz), 6.28 (1H, dd, J= 5.5, 3.1 Hz); IR(KCl, liquid film, major): 2987, 1453, 1343, 1196, 1049, 967, 706 cm^{-1}.
MS: 286(M^+, $C_{11}H_8F_6O_2^+$). Anal. Calc. for $C_{11}H_8F_6O_2$: C, 46.17; H, 2.82; F, 39.83%. Found: C, 45.86; H, 2.77, F, 39.88%.

Polymer 4. ^{19}F NMR (δ, THF-d8) -77 to - 87 (5 F from 1b), -95 to -124 (4 F from TFE, 2.5 F from **1b**), -128 to - 134 (2.5 F from **1b**). By integration, the polymer

composition was calculated to be 54 % TFE and 46 % **1b**. Anal. Found: C, 36.54; H, 1.61; F, 57.01.

Polymer 5. ^{19}F NMR (δ, $CDCl_3$) -68.5 and -74.0 (3F, isomeric CF3 groups from 1c), -95 to -125 (4F from TFE and 2F from **1c**. By integration, the polymer composition was calculated to be 52 % TFE and 48 % **1c**. Anal. Found: C, 47.77; H, 4.00; F, 42.04.

Polymer 6. ^{19}F NMR (δ, $CDCl_3$) -66.83 (3F from **1d**), -75.42 (3F from **1d**), -95 to -125 (4F from TFE). By integration, the polymer composition was calculated to be 45 % TFE and 55 % **1d**. Anal. Found: C, 45.85; H, 3.00; F, 49.26.

Polymer 7. ^{19}F NMR (δ, THF-d8) -72.9 (6F from **1e**), -95 to -125 (4F from TFE), -142.3 and -168.3 (1F from **1e**). By integration, the polymer composition was calculated to be 40 % TFE and 60 % **1e**. Anal. Found: C, 45.99; H, 3.88; F, 40.95.

Polymer 8. ^{19}F NMR (δ, THF-d8) -60.3, -67.8 and -71.5 (9F from **1f**), -95 to -125 (4F from TFE). By integration, the polymer composition was calculated to be 45 % TFE and 55 % **1f**. Anal. Found: C, 41.87; H, 2.95; F, 49.76.

Polymer 9. ^{19}F NMR (δ, THF-d8) -70.6 and -72.5 (6F from **1g**), -95 to -125 (4F from TFE and 2 F from **1g**), -157.9 and -184.7 (1F from **1g**). By integration, the polymer composition was calculated to be 47 % TFE and 53 % **1g**. Anal. Found: C, 39.57; H, 2.47; F, 53.05

Polymer 10. ^{19}F NMR (δ, THF-d8) -73.4 and -79.4 (3F from **1h**), -95 to -125 (4F from TFE and 2F from **1h**). By integration, the polymer composition was calculated to be 43 % TFE and 57 % **1h**. Anal. Found: C, 40.49; H, 2.49; F, 44.86.

Polymer 11. ^{19}F NMR (δ, THF-d8) -75.7 (12F from **1i**), -95 to -125 (4F from TFE). By integration, the polymer composition was calculated to be 53 % TFE and 47 % **1i**. Anal. Found: C, 39.10; H, 2.83; F, 45.81.

Polymer 12. ^{19}F NMR (δ, THF-d8) -75 to -85 (2F from **1j**), -95 to -125 (4F from TFE and 4.5 F from **1j**), -132.0 (0.5F from **1j**), +44.7 (SO_2F, 1F from **1j**). By integration, the polymer composition was calculated to be 53 % TFE and 47 % **1j**. Anal. Found: C, 33.42; H, 1.91; F, 42.37

Polymer 13. ^{19}F NMR (δ, THF-d8) -75 to -90 (7F from **1k**), -95 to -125 (5F from 1k and 4F from TFE), -147 (1F from **1k**) +42 (1F from **1k**). Anal. Found: C, 30.65; H, 1.46; F, 47.47

Polymer 14. ^{19}F NMR (δ, THF-d8) -68.6 and -78.9 (6F from **2a**), -95 to -125 (4F from TFE). By integration, the polymer composition was calculated to be 49 % TFE and 51 % **2a**. Anal. Found: C, 41.04; H, 2.52; F, 49.73.

Polymer 15. ^{19}F NMR (δ, THF-d8) +44.0 (1F from **2b**), -95 to -125 (4F from TFE and 3F from **2b**). By integration, the polymer composition was calculated to be 48 % TFE and 52 % **2a**. Anal. Found: C, 37.32; H, 2.39; F, 36.41.

Polymer 16. ^{19}F NMR (δ, THF-d8) -57.4 (6F from **2c**), -95 to -125 (4F from TFE). By integration, the polymer composition was calculated to be 48 % TFE and 52 % **2c**. Anal. Found: C, 43.06; H, 2.10; F, 48.91.

Polymer 17. ^{19}F NMR (δ, THF-d8) -68.1 (3F from **2d**), -70.2 (3F from **2d**), -95 to -125 (4F from TFE). By integration, the polymer composition was calculated to be 48 % TFE and 52 % **2d**. Anal. Found: C, 41.22; H, 2.47; F, 47.98.

Polymer 18. ^{19}F NMR (δ, THF-d8) -77.6 (6F from NB-F-OH), -95 to -125 (4F from TFE and 2F from **1l**), -160 and -187 (1F from **1l**). Anal. Found: C, 46.10; H, 3.86; F, 39.14.

Polymer 19. ^{19}F NMR (δ, THF-d8) -75.7 (6F from NB-F-OH), -95 to -125 (4F from TFE), -169 (1F from **1m**). Anal. Found: C, 48.14; H, 4.34; F, 36.48.

Polymer 20-1. ^{19}F NMR (δ, THF-d8) -77.0 (6F from NB-F-OH), -65.4 and -66.6 (3F from one isomer of **1n**), -74.4 and -75.9 (3F from second isomer of **1n**) (isomers present in a 47:53 ratio), -95 to -125 (4F from TFE). Anal. Found: C, 43.58; H, 3.60; F, 42.70.

Polymer 21. ^{19}F NMR (δ, THF-d8) -77.5 (6F from NB-F-OH), -95 to -125 (4F from TFE). ^{13}C NMR (δ, CD_2Cl_2) (selected absorptions used for analysis) 64.75 (OCH_2 from NB-F-OH), 105.88 to 132.7 (quartet from CF_3 groups of NB-F-OH overlapping envelope from TFE), 164.6 to 177.8 (C=O from **1o**). Anal. Found: C, 51.52; H, 4.72; F, 32.53.

Polymer 22. ^{19}F NMR (δ, THF-d8) -77.0 (6F from NB-F-OH), -70.5 and -71.5 (6F from **1p**), -95 to -125 (4F from TFE). Anal. Found: C, 43.18; H, 3.61; F, 42.43.

Polymer 23-1. ^{19}F NMR (δ, THF-d8) -77.0 (6F from NB-F-OH), -95 to -125 (4F from TFE). ^{13}C NMR (δ, CD_2Cl_2) (selected absorptions used for analysis) 64.4 (OCH_2 from NB-F-OH), 105.88 to 132.7 (quartet from CF_3 groups of NB-F-OH overlapping envelope from TFE), 172 to 178 (C=O from **1q**). Anal. Found: C, 47.73; H, 4.11; F, 34.50.

Polymer 24-2. Anal. Found: C, 53.48; H, 5.11; F, 30.81.

Polymer 24-3. Anal. Found: C, 55.33; H, 5.42; F, 28.14.

Polymer 24-4. Anal. Found: C, 56.83; H, 5.87; F, 24.67.

Polymer 25. ^{19}F NMR (δ, DMSO-d6) -124.5 (2F from **1a**), -95 to -123 (4F from TFE and 2F from **1a**), -77.0 (6F from NB-F-OH). ^{13}C NMR (δ, DMSO-d6) (selected

absorptions used for analysis) 110 to 130 (2C from TFE, 2C from NB-F-OH, 2C from 1a), 62.5 to 69.9 (1C from NB-F-OH, 1C from HAdA), 165 to 178 (1C from PinAc, 1C from HAdA). Anal. Found: C, 54.26; H, 6.37; F, 22.74.

Polymer 26. ^{19}F NMR (δ, DMSO-d6) -58 and -82 (3F from **1h**), -95 to -125 (4F from TFE and 2 F from **1h**). ^{13}C NMR (δ, DMSO-d6) (selected absorptions used for analysis) 110 to 130 (2C from TFE and 2 C from **1h**), 166 and 174 (C=O from acrylate). Anal. Found: C, 48.33; H, 4.24; F, 36.76.

Polymer 27. ^{19}F NMR (δ, DMSO-d6) -58 and -82 (3F from **1h**), -95 to -125 (4F from TFE and 2 F from **1h**). ^{13}C NMR (δ, DMSO-d6) (selected absorptions used for analysis) 110 to 130 (2C from TFE and 2 C from **1h**), 72.6 (1C from PinAc), 68.6 (1C from HAdA), 166 and 174 (C=O from three acrylates, MAdA determined from difference). Anal. Found: C, 57.61; H, 5.96; F, 21.49.

Polymer 28. ^{19}F NMR (δ, DMSO-d6) -58 and -82 (3F from **1h**), -95 to -125 (4F from TFE and 2 F from **1h**). ^{13}C NMR (δ, DMSO-d6) (selected absorptions used for analysis) 110 to 130 (2C from TFE and 2 C from **1h**), 72.6 (1C from PinAc), 68.6 (1C from HAdA). Anal. Found: C, 55.69; H, 5.94; F, 22.29.

Polymer 29. ^{19}F NMR (δ, DMSO-d6) -77.0 (6F from NB-F-OH), -68.2 and -69.9 (6F from **1p**), -95 to -125 (4F from TFE). ^{13}C NMR (δ, DMSO-d6) (selected absorptions used for analysis) 110 to 130 (2C each from TFE, NB-F-OH and **1p**), 84.8 to 89.6 (1C from PinAc), 68.3 (1C from HAdA). Anal. Found: C, 53.84; H, 5.66; F, 23.52.

Polymer 30-1. ^{19}F NMR (δ, DMSO-d6) -77.0 (6F from NB-F-OH), -95 to -125 (4F from TFE). ^{13}C NMR (δ, DMSO-d6) (selected absorptions used for analysis) 110 to 130 (2C from TFE and 2 C from NB-F-OH), 60 to 71 (1C from HAdA and 1 C from NB-F-OH), 166 and 174 (C=O, 1 C from HAdA, 2C from **1q**). Anal. Found: C, 50.19; H, 5.14; F, 30.00.

Polymer 30-2. Anal. Found: C, 51.72; H, 5.54; F, 27.36.

Polymer 31. ^{19}F NMR (δ, DMSO-d6) -77.0 (6F from NB-F-OH), -95 to -125 (4F from TFE). ^{13}C NMR (δ, DMSO-d6) (selected absorptions used for analysis) 110 to 130 (2C from TFE and 2C from NB-F-OH), 61 to 71 (1C from NB-F-OH and 2 C from GBLA), 166 and 174 (C=O, 2C from GBLA, 2C from **1q**). Anal: Found: C, 46.17; H, 4.07; F, 33.06.

Polymer 32. ^{19}F NMR (δ, DMSO-d6) -77.0 (6F from NB-F-OH), -95 to -125 (4F from TFE). ^{13}C NMR (δ, DMSO-d6) (selected absorptions used for analysis) 110 to 130 (2C from TFE and 2C from NB-F-OH), 178.6 (lactone C=O from NBLA), 166 and 174 (C=O, 1C from NBLA, 2C from **1q**). Anal. Found: C, 48.43; H, 4.33; F, 31.81.

Polymer 33. ^{19}F NMR (δ, CD_2Cl_2) -77.0 (6F from NB-F-OH), -95 to -125 (4F from TFE). ^{13}C NMR (δ, CD_2Cl_2) (selected absorptions used for analysis) 110 to 130 (2C from TFE and 2C from NB-F-OH), 64.6 (1C from NB-F-OH), 70 (1C from HAdA), 89.6 (1C from PinAc) 166 and 174 (C=O, 1C from HAdA, 1C from PinAc, 2C from **1q)**. Anal. Found: C, 57.25; H,
6.81: F, 18.13.

Polymer 34. ^{19}F NMR (δ, CD_2Cl_2) -77.0 (6F from NB-F-OH), -95 to -125 (4F from TFE). ^{3}C NMR (δ, CD_2Cl_2) (selected absorptions used for analysis) 110 to 130 (2C from TFE and 2C from NB-F-OH), 64.6 (1C from NB-F-OH), 70 (1C from HAdA), 166 - 180 (C=O, 1C from t-BuAc, 1C from HAdA, 2C from **1q**). Anal. Found: C, 57.15; H, 6.63; F, 18.54.

Polymer 35. ^{19}F NMR (δ, CD_2Cl_2) -77.0 (6F from NB-F-OH), -95 to -125 (4F from TFE). ^{13}C NMR (δ, CD_2Cl_2) (selected absorptions used for analysis) 110 to 130 (2C from TFE and 2C from NB-F-OH), 64.6 (1C from NB-F-OH), 70 (1C from HAdA),

87.8 (1C from MAdA) 166 - 180 (C=O, 1C from MAdA, 1C from HAdA, 2C from **1q)**. Anal. Found: C, 58.66; H, 6.58; F, 18.75.

Polymer 36. ^{19}F NMR (δ, DMSO-d6) -77.0 (6F from NB-F-OH), -95 to -125 (4F from TFE). ^{13}C NMR (δ, DMSO-d6) (selected absorptions used for analysis) 110 to 130 (2C from TFE and 2C from NB-F-OH), 89.3 (1C from PinAc), 62 to 71 (1C from NB-F-OH and 2 C from GBLA), 166 and 174 (C=O, 2C from GBLA, 1C from PinAc, 2C from **1q**). Anal. Found: C, 53.25; H, 5.90; F, 17.97.

Polymer 37. ^{19}F NMR (δ, DMSO-d6) -77.0 (6F from NB-F-OH), -95 to -125 (4F from TFE). ^{13}C NMR (δ, DMSO-d6) (selected absorptions used for analysis) 110 to 130 (2C from TFE and 2C from NB-F-OH), 89.3 (1C from MAdA), 62 to 71 (1C from NB-F-OH and 2 C from GBLA), 166 and 174 (C=O, 2C from GBLA, 1C from MAdA, 2C from **1q**). Anal. Found: C, 56.15; H, 6.29; F, 17.47.

Polymer 38. ^{19}F NMR (δ, DMSO-d6) -77.0 (6F from NB-F-OH and 12F from NB-di-F-OH), -95 to -125 (4F from TFE). ^{13}C NMR (δ, DMSO-d6) (selected absorptions used for analysis) 110 to 130 (2C from TFE, 2C from NB-F-OH and 4 C from NB-diF-OH), 65.96 (1C from NB-F-OH), 170.4 (1C from **1q**), 161.2 to 168.4 and 171.7 to 177 (1C from HAdA and 1C from **1q**). Anal. Found: C, 51.65; H, 5.12; F, 28.11.

Polymer 39-1. ^{19}F NMR (δ, DMSO-d6) -77.0 (6F from NB-F-OH), -95 to -125 (4F from TFE). ^{13}C NMR (δ, DMSO-d6) (selected absorptions used for analysis) 110 to 130 (2C from TFE and 2C from NB-F-OH), 61 to 70.7 (1C from HAdA and 1C from NB-F-OH), 166 to 178 (1C from HAdA and 2 C from **1r**). Anal. Found: C, 49.95; H, 4.99; F, 30.93.

Polymer 39-2. Anal. Found: C, 53.42; H, 5.43; F, 25.99.

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