Supporting information

A Novel Dual-tone Molecular Glass Resist Based on Adamantane Derivatives for Electron Beam Lithography

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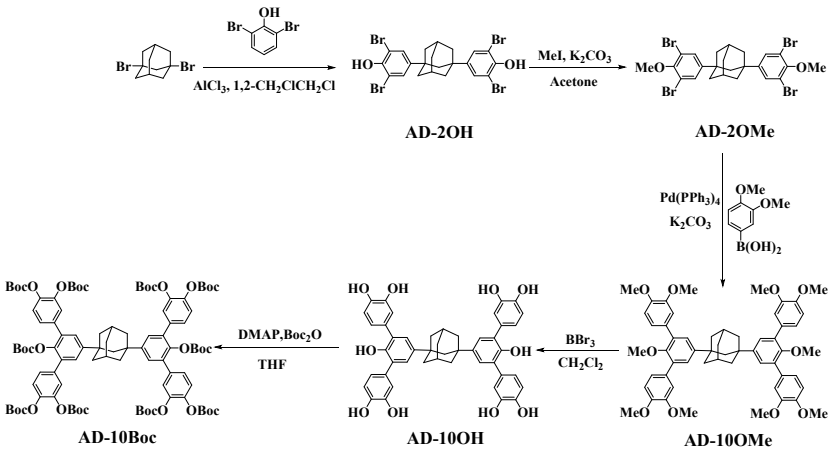
S1 Synthesis of materials



Scheme S1. The synthesis procedures of AD-10Boc

1.1 Synthesis of AD-2OH

A 250-mL two-neck round-bottom flask was fitted with a magnetic stirrer, a nitrogen inlet and an outlet running to an alkaline liquid. 2,6-dibromophenol (19 g, 75 mmol), 1,3-dibromoadamantane (8.89 g, 30 mmol) and anhydrous 1, 2-dichloroethane (30 mL) were added into the flask placed in an ice-bath. And then the powder of anhydrous aluminum chloride (1.3 g, 0.9 mmol) was added in four portions over 20 minutes to the chilled, stirring solution. The mixture was kept in an ice-bath for 6 hours and then quenched with acidic water. Through filtering, the precipitates were obtained and washed by dichloromethane for three times. Upon recrystallization from acetone, A white solid was isolated: 11.3g (57.8%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (s, 4H, benzene), 5.75 (s, 2H, Ar-OH), 2.32 (s, 2H, adamantane), 1.87 (s, 10H, adamantane), 1.75 (s, 2H, adamantane). HRMS (ESI) m/z: $[M-H]^-$ calcd for $C_{22}H_{19}Br_4O_2^-$ 634.8083, found 634.8079.

1.2 Synthesis of AD-2OMe

AD-2OH (15 g, 23 mmol), potassium carbonate (15.9 g, 115 mmol), iodomethane (21g, 115mmol) and anhydrous acetone (80 mL) were added to a 250-mL schlenk flask. Then the mixture was refluxed at 60 ℃ and stirred until complete conversion. The mixture was diluted with dichloromethane and washed with

brine. The organic layer was separated, dried over anhydrous sodium sulfate, filtered and then concentrated under reduced pressure. After removing the solvent, a white solid was obtained: (15.3 g, 95%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 (s, 4H, benzene), 3.87 (s, 6H, methoxy), 2.33 (s, 2H, adamantane), 1.91 – 1.84 (m, 10H, adamantane), 1.76 (s, 2H, adamantane). HRMS (ESI) m/z: $[M-CH_3]^-$ calcd for $C_{23}H_{21}Br_4O_2^-$ 648.8240, found 648.8240.

1.3 Synthesis of AD-10OMe

AD-2OMe (15.3 g, 23 mmol), 3,4-dimethoxylphenlboronic acid (21 g, 115 mmol), tetrakis-(triphenylphosphine)palladium (265.8 mg, 0.23 mmol) and 1,4-dioxone (60 mL) were added to a 250-mL schlenk flask. The mixture was degassed and then potassium carbonate (15.9 g, 115 mmol) dissolved in water (60 mL) was injected under nitrogen. The mixture was then refluxed at 110 ℃ for 8 hours. After the reaction was completed, the mixture was cooled to room temperature, diluted with dichloromethane and washed with brine. The organic layer was separated, dried over anhydrous sodium sulfate, filtered and then concentrated under reduced pressure. The crude products were purified by column chromatography on silica gel (dichloromethane /methanol = 60:1, v/v) to obtain AD-10OMe as a white solid (19 g, 95%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (s, 4H, benzene), 7.18 (s, 4H, benzene), 7.10 (d, J = 8.2 Hz, 4H, benzene), 6.94 (d, J = 8.0 Hz, 4H, benzene), 3.92 (d, J = 7.8 Hz, 24H, methoxy), 3.23 (s, 6H, methoxy), 2.35 (s, 2H, adamantane), 2.11 (s, 2H, adamantane), 2.07 – 1.98 (m, 8H, adamantane), 1.80 (s, 2H, adamantane). HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{56}H_{60}O_{10}Na^+$ 915.4078, found 915.4079.

1.4 Synthesis of AD-10OH

AD-10MeO (2.0 g, 2.2 mmol) and dichloromethane (30 mL) were added to a 250-mL two-necked flask and cooled to -78 ℃ with a dry ice/acetone cooling bath. Then boron tribromide (3.8 g, 15.4 mmol) dissolved in dichloromethane (30 mL) was slowly introduced through a dropping funnel for 30 min. After

addition, the reaction mixture was stirred for 6 hours at room temperature and quenched by slow addition of water (10 mL) to give a white precipitate. The precipitate was filtered and washed with water and dichloromethane thoroughly to give the product AD-10OH as a white solid (1.6 g, 95%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.87 (d, J = 21.6 Hz, 8H, Ar-OH), 7.63 (s, 2H, Ar-OH), 7.04 (s, 4H, benzene), 6.92 (s, 4H, benzene), 6.76 (s, 8H, benzene), 2.24 (s, 2H, adamantane), 2.07 – 1.89 (m, 6H, adamantane), 1.84 (d, J = 11.2 Hz, 4H, adamantane), 1.72 (s, 2H, adamantane). HRMS (ESI) m/z: $[M-H]^-$ calcd for $C_{46}H_{39}O_{10}^-$ 751.2549, found 751.2545.

1.5 Synthesis of AD-10Boc

AD-10OH (1.6 g, 2.1 mmol), Boc_2O (6.9 g, 31.5 mmol), 4-dimethylaminopyridine (51.2 mg, 0.42 mmol) and tetrahydrofuran (30 mL) were added to a 100-mLflask. Then the mixture was heated at 50 ℃ for 8 hours. After the reaction was completed, the mixture was cooled to room temperature, diluted with dichloromethane and washed with brine. The organic layer was separated, dried over anhydrous sodium sulfate, filtered and then concentrated under reduced pressure. The crude products were purified by column chromatography on silica gel (petroleum ether/ethyl acetate=6:1, v/v) to obtained AD-10Boc as a white spumescent solid (3 g, 81.1%). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.38 (s, 4H, benzene), 7.34 (d, J = 8.3 Hz, 8H, benzene), 7.29 (d, J = 8.6 Hz, 4H, benzene), 2.35 (s, 2H, adamantane), 2.05 - 1.94 (m, 10H, adamantane), 1.78 (s, 2H, adamantane), 1.54 (d, J = 6.5 Hz, 72H, -$OC(CH_3)_3$), 1.18 (s, 18H, -$OC(CH_3)_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.02, 150.60, 150.53, 148.54, 143.02, 142.12, 141.96, 136.40, 133.82, 127.33, 127.26, 123.90, 122.86, 83.63, 83.53, 83.37, 42.10, 37.39, 29.45, 27.65, 27.12. FT-IR (KBr): 2981.7, 2932.8, 1768.5, 1507.4, 1395.9, 1371.2, 1286.0, 1256.5, 1154.4, 1113.3, 1049.8, 1013.1, 891.8, 831.2, 773.7, 737.0. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{96}H_{120}O_{30}Na^+$ 1776.7790, found 1776.7740.

S2 NMR, FT-IR and HR-MS spectra of compounds

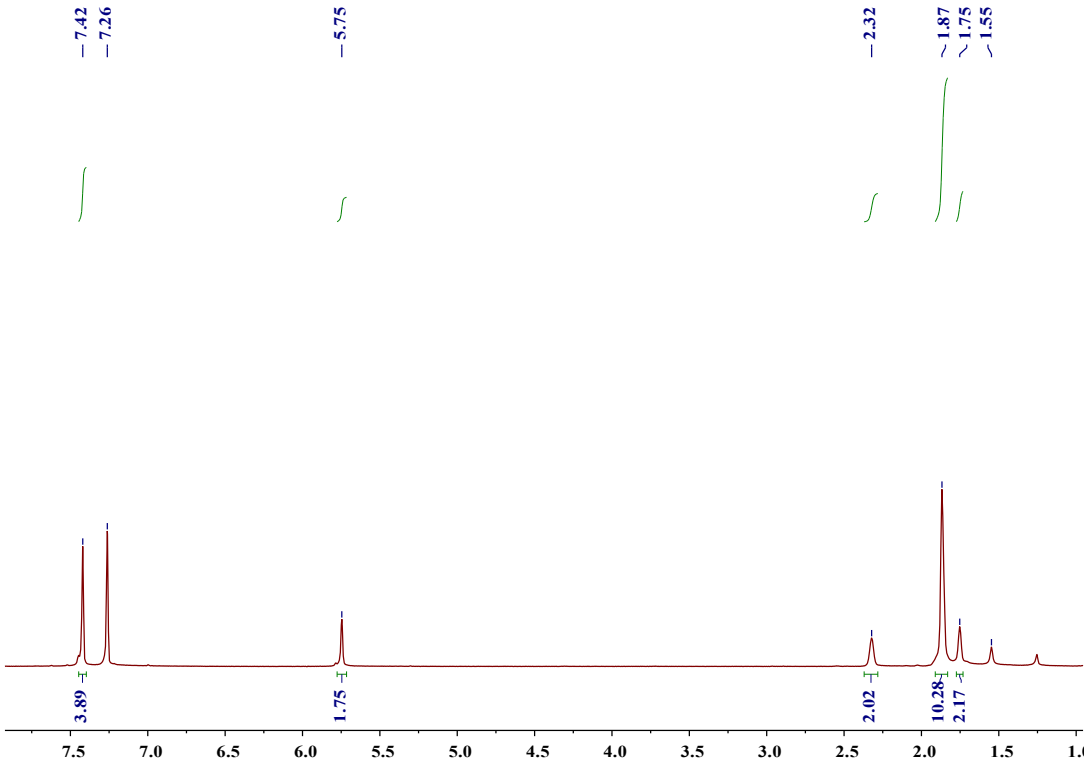


Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of AD-2OH.

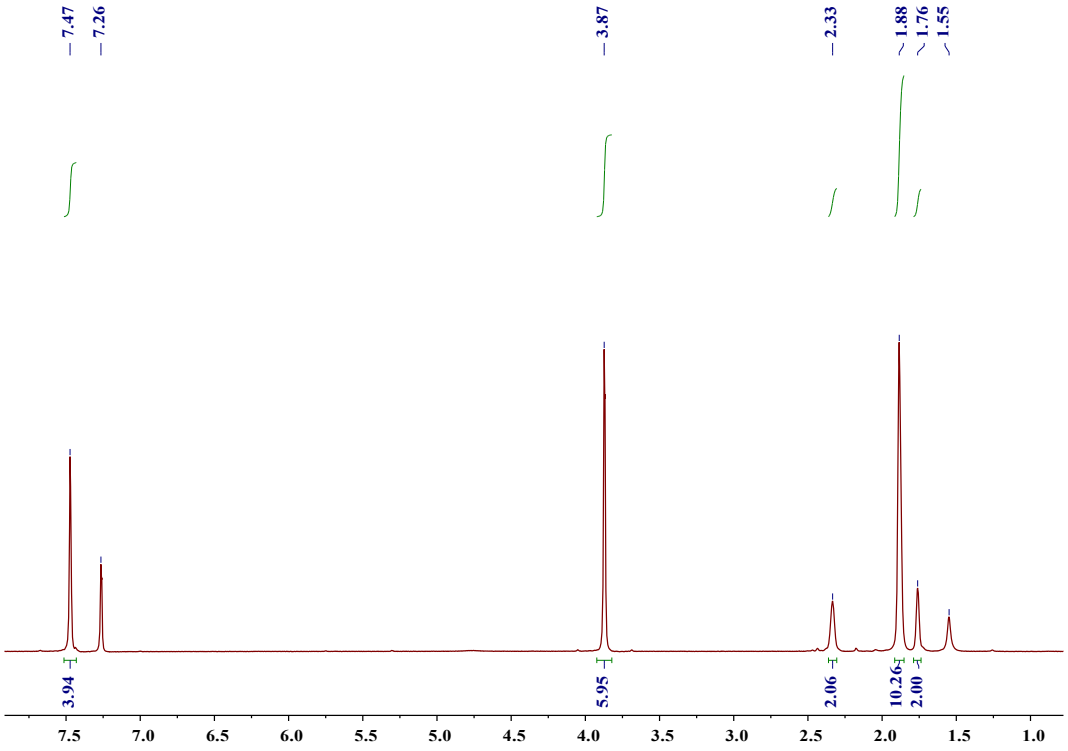


Figure S2. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of AD-2OMe.

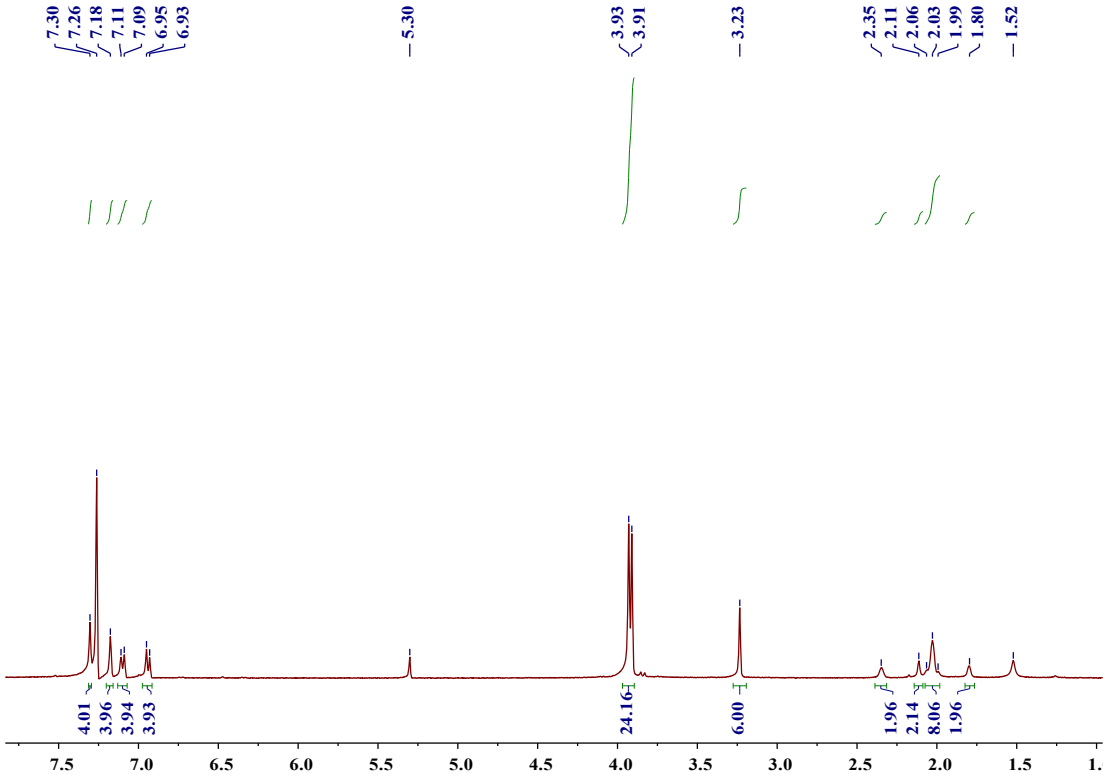


Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of AD-10OMe.

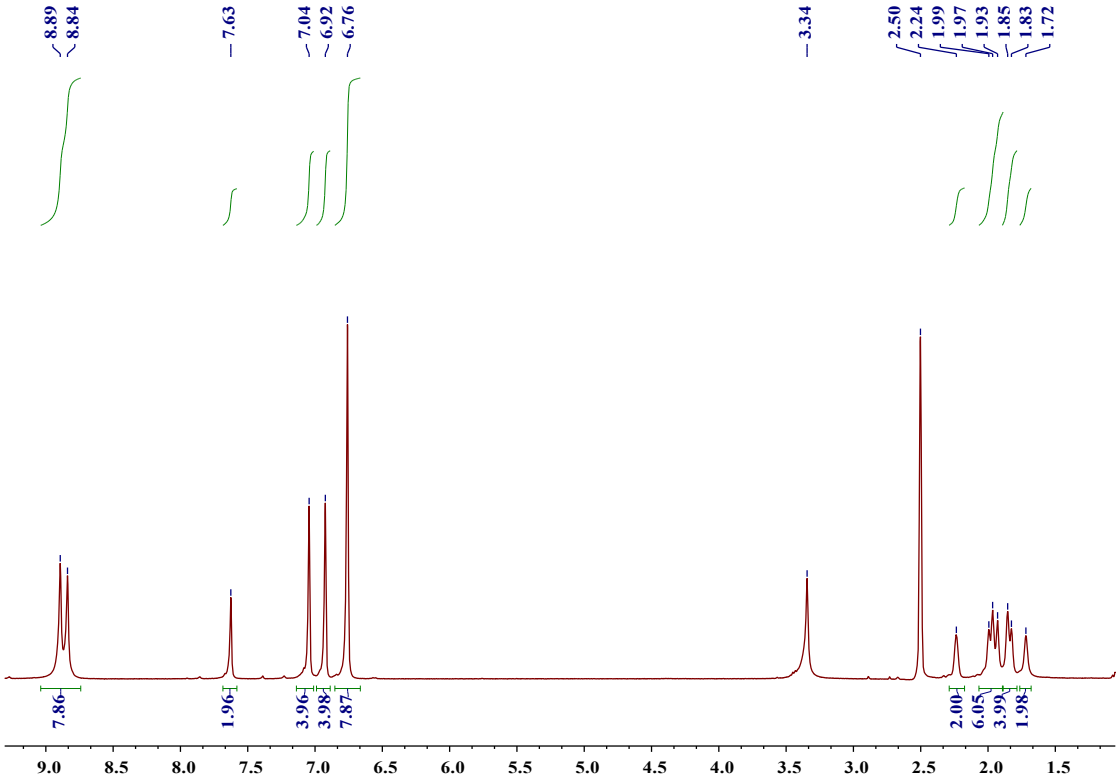


Figure S4. ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of AD-10OH.

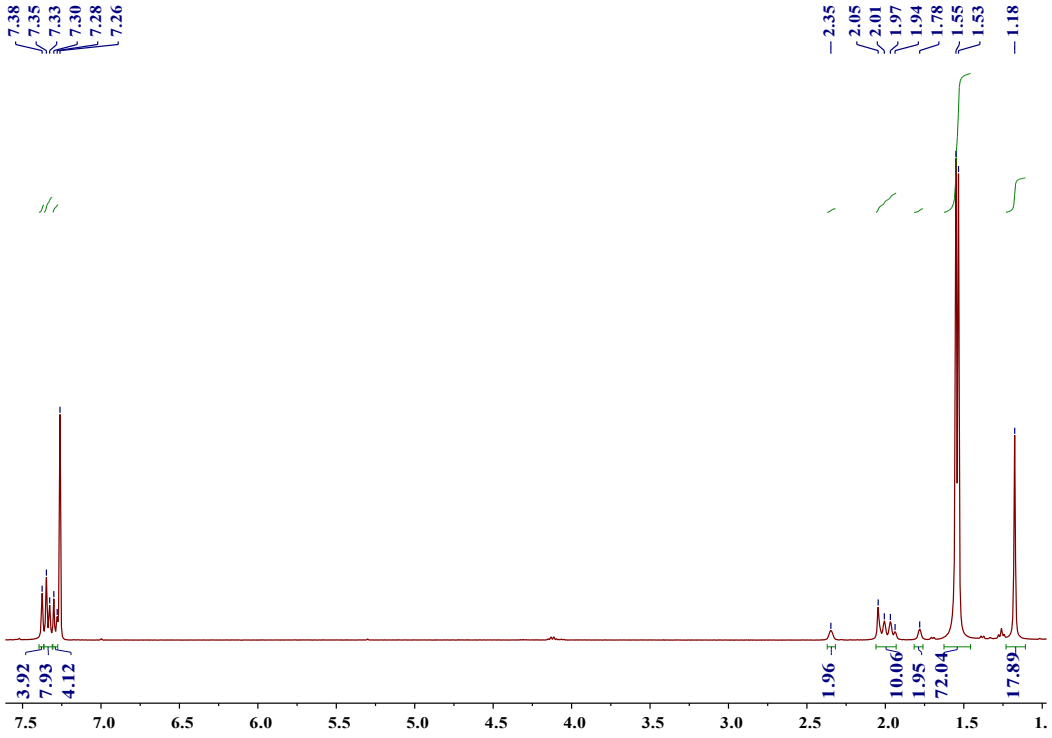


Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of AD-10Boc.

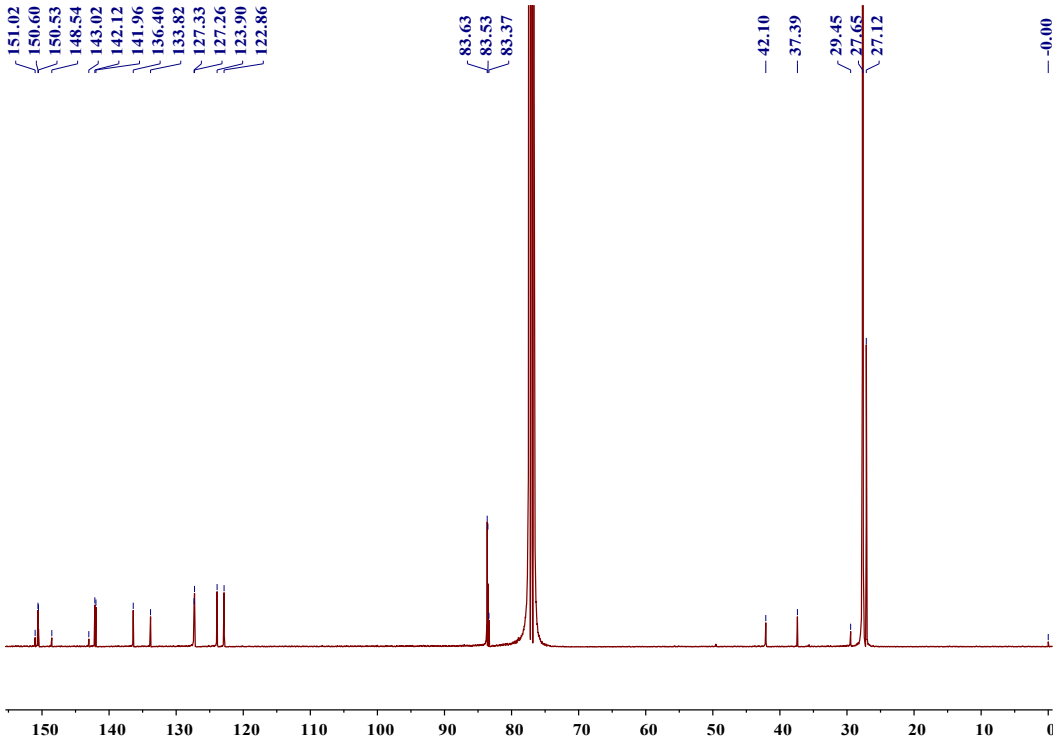


Figure S6. ^{1}C NMR (400 MHz, $CDCl_3$) spectrum of AD-10Boc.

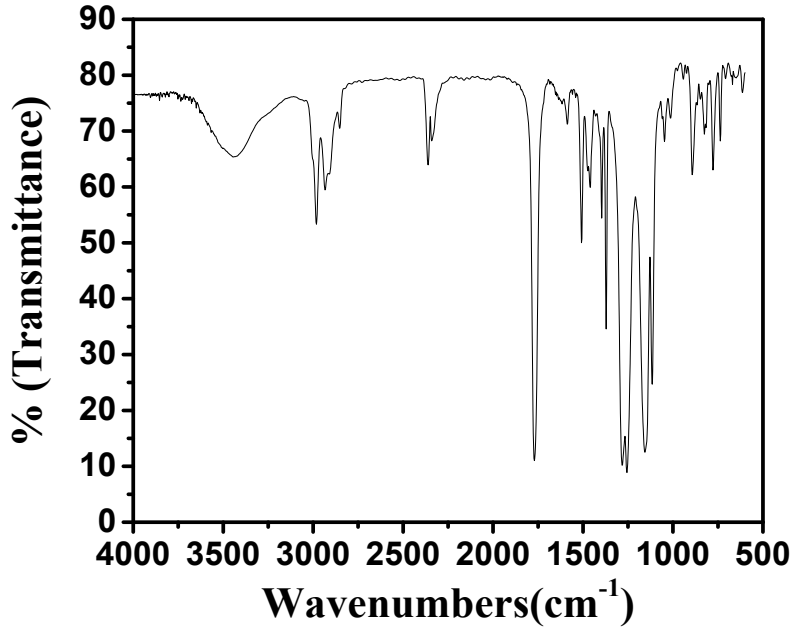


Figure S7. FT-IR spectrum of AD-10Boc.

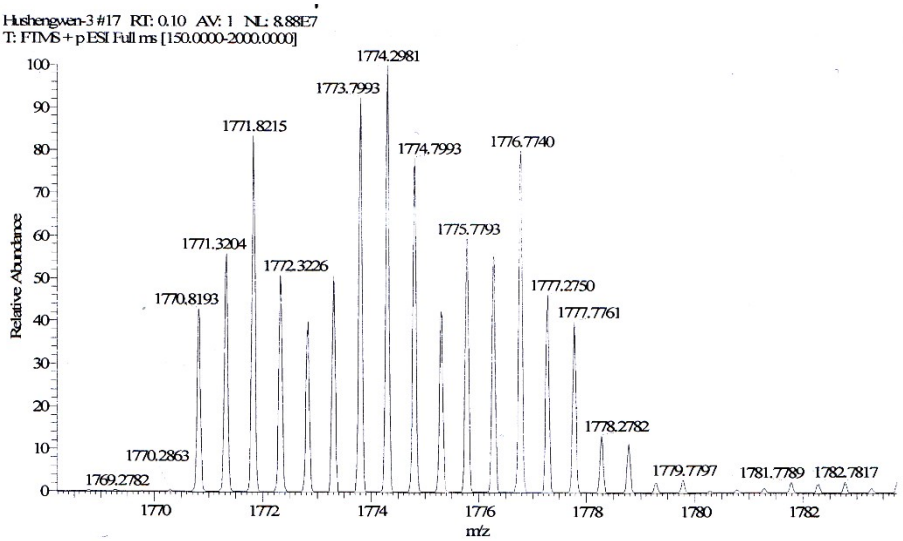


Figure S8. HR-ESI spectrum of AD-10Boc.

S3 The solubility of AD-10Boc and AD-10OH

Table S1 Solubility of AD-10OH and AD-10Boc

Solvent	AD-10OH	AD-10Boc
Water	-	-
DMSO	++	++
Ethanol	++	++
THF	++	++
Acetone	++	++
Ethyl acetate	++	++
Dichloromethane	-	++
PGMEA	++	++
Toluene	-	++
Cyclohexanone	++	++
Chlorocyclohexane	-	++
Anisole	-	++
n-Hexane	-	++
cyclohexane	-	++
2.38wt%TMAH solution	++	-

++: soluble at room temperature; +-: partly soluble; -: insoluble

S4 The SEM image of AD-10Boc film

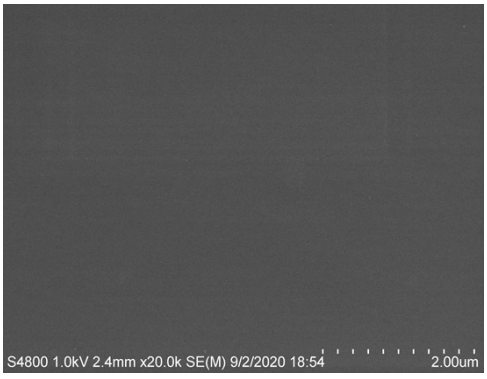


Figure S9. SEM image of AD-10Boc film.

S5 The lithographic patterns of AD-10Boc resist under different developing times

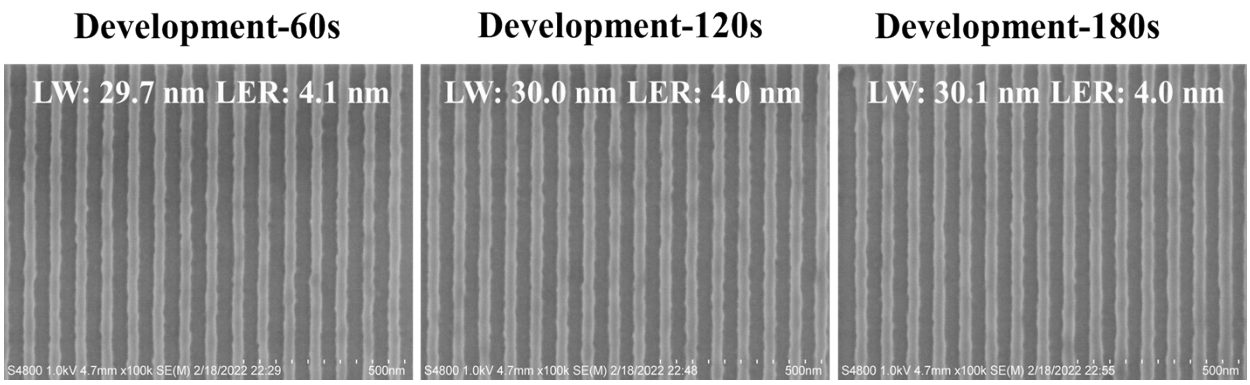


Figure S10. High-resolution SEM images of line-space patterns (top view) for AD-10Boc resist at different developing times (Developing times: 60, 120 and 180 s).

S6 The AFM images of AD-10Boc resist upon the exposure of EBL

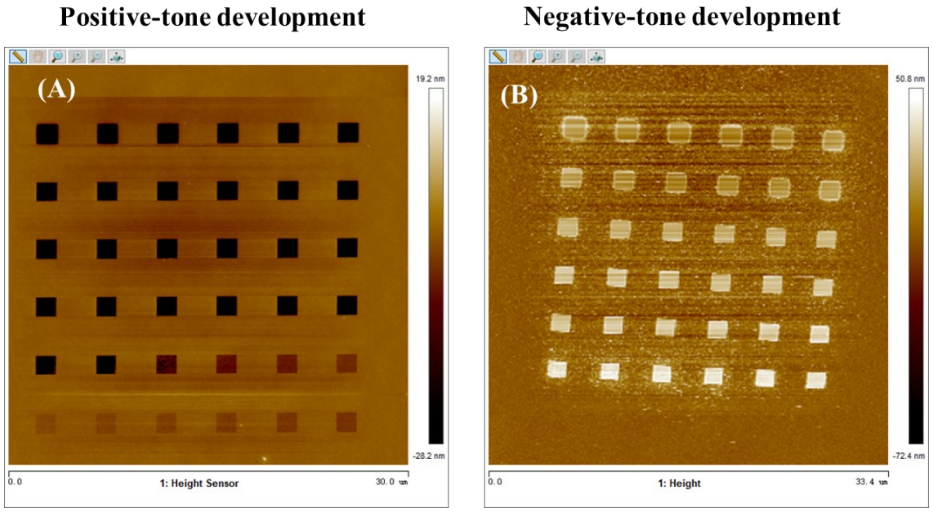
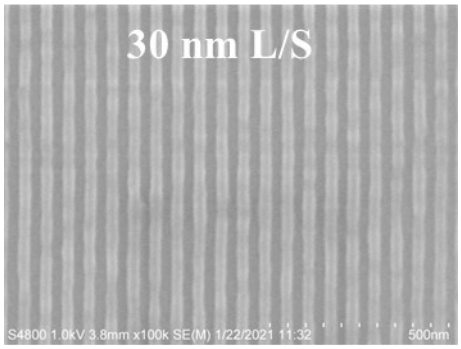


Figure S11. Atomic force micrograph of AD-10Boc resist patterns at different exposure doses. (A) Positive-tone development, (B) Negative-tone development

S7 The Patterning properties of 950k PMMA



Dose: 740μC/cm²
LER: 3.0 nm

Figure S12. High-resolution e-beam patterning image of 950k PMMA*

* The exposure parameter settings of 950k PMMA is the same as that of AD-10Boc resist.

The Z-parameter for 950k PMMA is 1.80×10^{-6} μC·nm³.