Supplementary Information

Increasing the sensitivity of non-chemically amplified molecular resist by a cascade esterification

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1. Synthesis and characterization of ADTPS

Synthesis of ADOMe: ADBr (5g,1eq,7.5mmol), phenylboronic acid (5.5g, 6eq, 45 mmol), tetrakis-(triphenylphosphine)palladium (175 mg, 0.02 eq, 0.15 mmol) and 1,4-dioxone (60 mL) were added to a 250-mL schlenk flask. The mixture was degassed and then potassium carbonate (6.25 g, 6eq, 45 mmol) dissolved in water (30 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 (Eluent: dichloromethane /petroleum ether = 1:2, v/v) to obtain ADOMe as a white solid (3.77g, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (m, 8H, benzene), 7.44 (m, 8H, benzene), 7.36 (m, 8H, benzene), 3.17 (s, 6H, methoxy), 2.36 -1.81 (m, 14H, adamantane).

Synthesis of ADOH: ADOMe (2.0 g,1eq, 3 mmol) and anhydrous dichloromethane (30 mL) were added to a 100-mL two-necked flask and cooled to 0 ℃. Then boron tribromide (3 g, 4eq, 12 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 ADOH as a white solid (1.43 g, 75%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.06 (s, 2H, phenolic hydroxy), δ 7.53 (m, 8H, benzene), 7.42 (m, 8H, benzene), 7.34 (m, 4H, benzene), 7.21 (s, 4H, benzene), 2.24 - 1.71 (m, 14H, adamantane).

Synthesis of ADBL. ADBL was synthesized with a similar method reported in the literature[1]. ADOH (1.2 g,1eq, 1.9 mmol), potassium carbonate (0.72 g,3eq, 5.7mmol) and dry acetone (20 mL) were added to a 100-mL three-necked flask, α-bromo-γ-butyrolactone (0.54 mL,3eq, 5.7mmol) was slowly introduced through a dropping funnel for 30 min. After addition, the reaction mixture was stirred for 12 hours under refluxed condition. 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 (Eluent: ethyl acetate /petroleum ether =1:4-1:1.5, v/v) to obtain ADBL as a white solid (0.6 g, 40%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.58 (m, 8H, benzene), 7.44 (m, 8H, benzene), 7.38 (m, 8H, benzene), 3.86(t, 2H, lactone), 3.80 (t, 2H, lactone), 3.55 (m, 2H, lactone), 2.27 -1.75 (m, 14H, adamantane), 1.82(m, 2H, lactone), 1.51 (m, 2H, lactone). HRMS (MALDI): calcd for $C_{54}H_{48}O_6K^+$ ([M+K]$^+$) 831.97, found 831.3085.

Synthesis of ADTPS. NaOH (0.14g, 2eq, 12.39mmol) dissolved in methanol (5 mL), triphenylsulfonium hydroxide (1 g, 2eq, 3.54mmol) dissolved in mixed solution of methanol (5 mL) and dichloromethane (5 mL) were added to a 100-mL two-necked, ADBL (1.4g,1eq, 1.77mmol) and dichloromethane (20 mL) was slowly introduced through a dropping funnel for 30 min. After addition, the reaction mixture was stirred for 5 hours under refluxed condition. After the reaction was completed, diluted with dichloromethane and washed with water three times. Collect the organic layers and concentrate in reduced pressure. Redissolve the crude product in dichloromethane and precipitation in ethyl acetate for two times and precipitation in ether for three times (1g, 55%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.81 (m, 30H, benzene), 7.65 (m, 8H, benzene), 7.35 (m, 8H, benzene), 7.24 (m, 8H, benzene), 3.56 (dd, 2H), 3.06 (t, 2H), 2.81 (t, 2H), 2.25 -1.73 (m, 14H, adamantane), 1.23 (m, 2H), 1.14 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.30 , 150.57. 144.32, 139.87, 134.34, 131.35, 129.37, 127.85, 126.73, 126.49, 125.13, 81.09, 58.90, 48.93, 41.51, 36.53, 34.40, 29.09. HRMS (ESI): calcd for $C_{54}H_{50}O_8^{2-}$ ([M^{2-}]) 413.1758, found 413.1755; calcd for $C_{18}H_{15}S^+$ ([M$^+$]) 263.0889, found 263.0890.

The ^{1}H NMR spectra of ADBL and ADTPS are shown in Figures S1 and S3. The high-resolution MALDI-TOF mass spectrum of ADBL is shown in Figure S2. The high-resolution ESI-TOF mass spectrum of ADTPS is shown in Figure S4. The FTIR spectra of ADBL and ADTPS is shown in Figure S5.

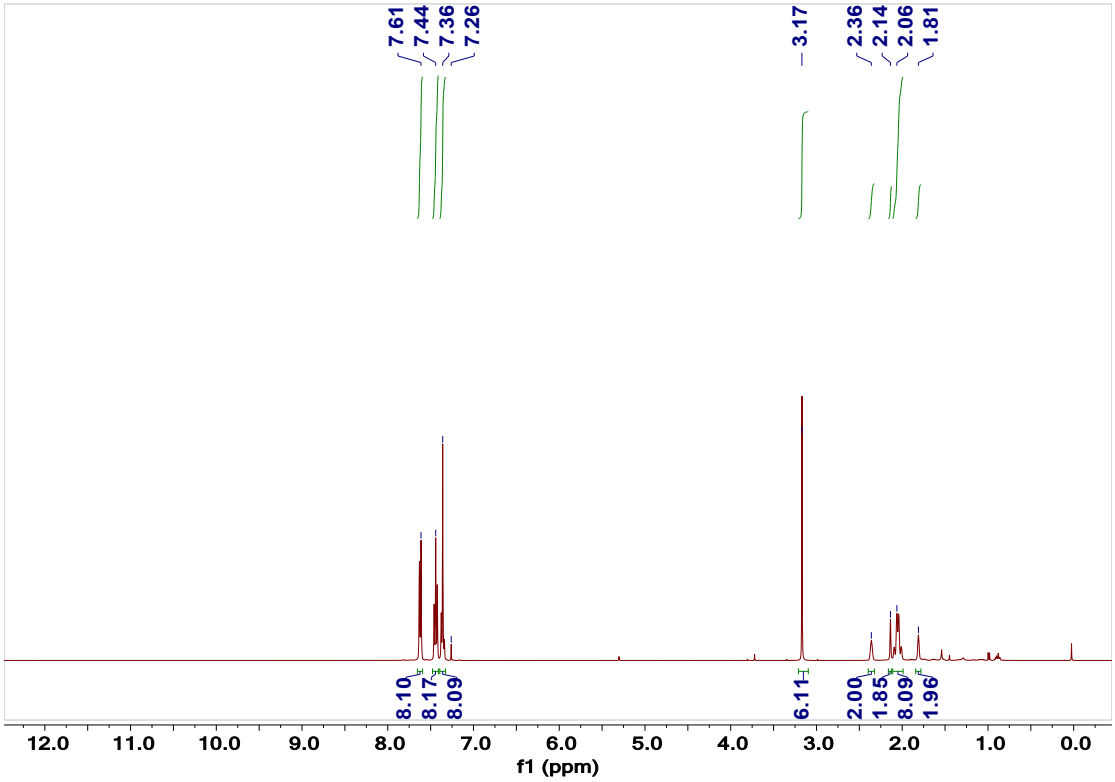

Figure S1. ^{1}H NMR spectrum of ADOMe. ($CDCl_3$, 400 MHz).

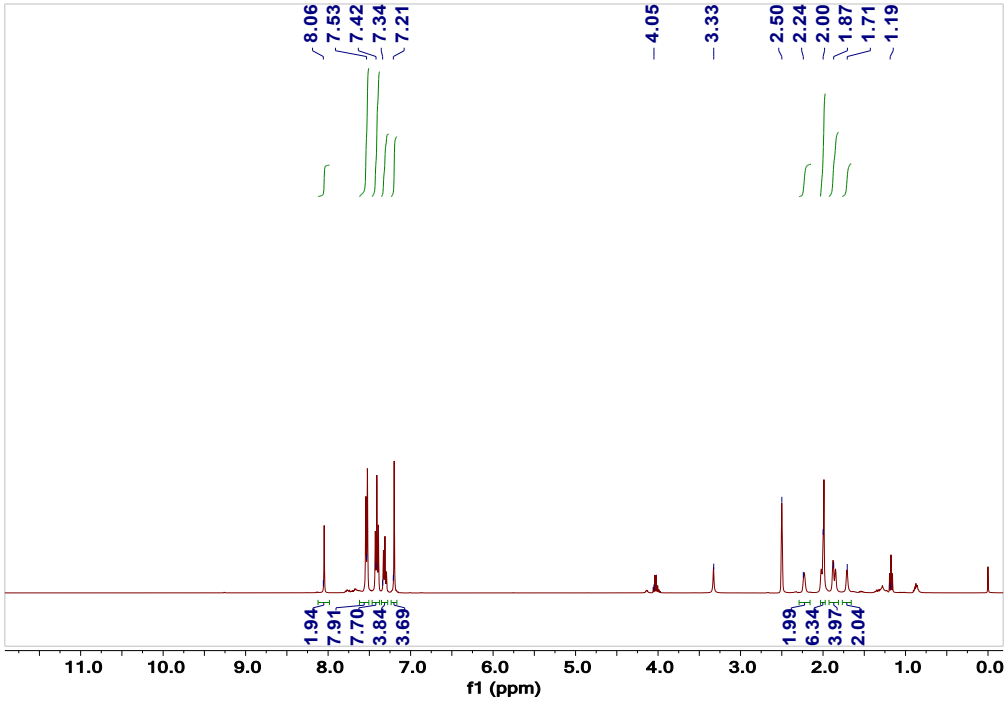

Figure S2. ^{1}H NMR spectrum of ADOH. (DMSO-d_6, 400 MHz).

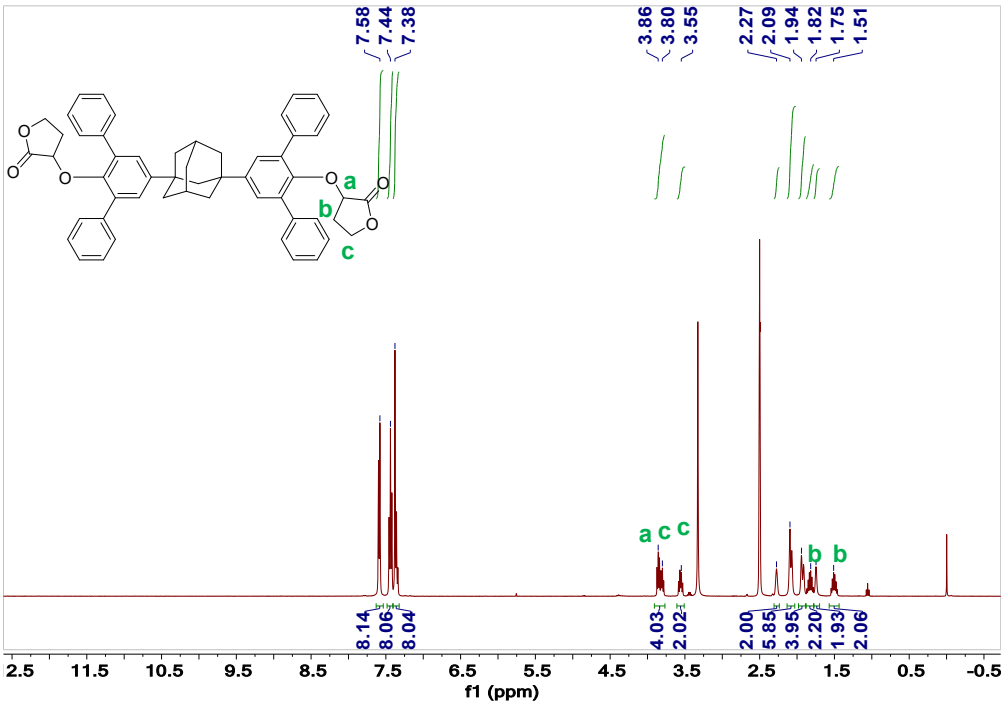

Figure S3. ^{1}H NMR spectrum of ADBL. (DMSO-d_6, 400 MHz).

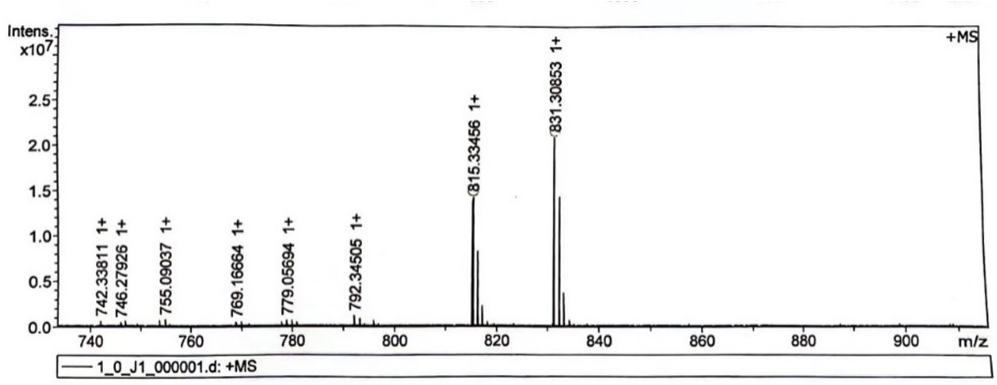

Figure S4. High-resolution MALDI mass spectrum of ADBL.

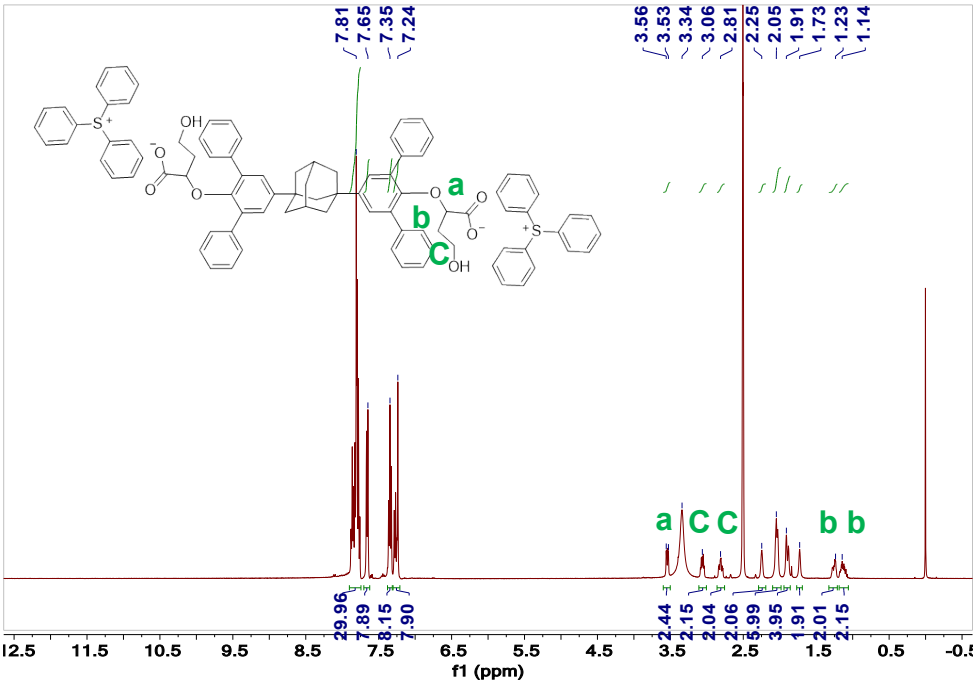

Figure S5. ^{1}H NMR spectrum of ADTPS. (DMSO-d_6, 400 MHz).

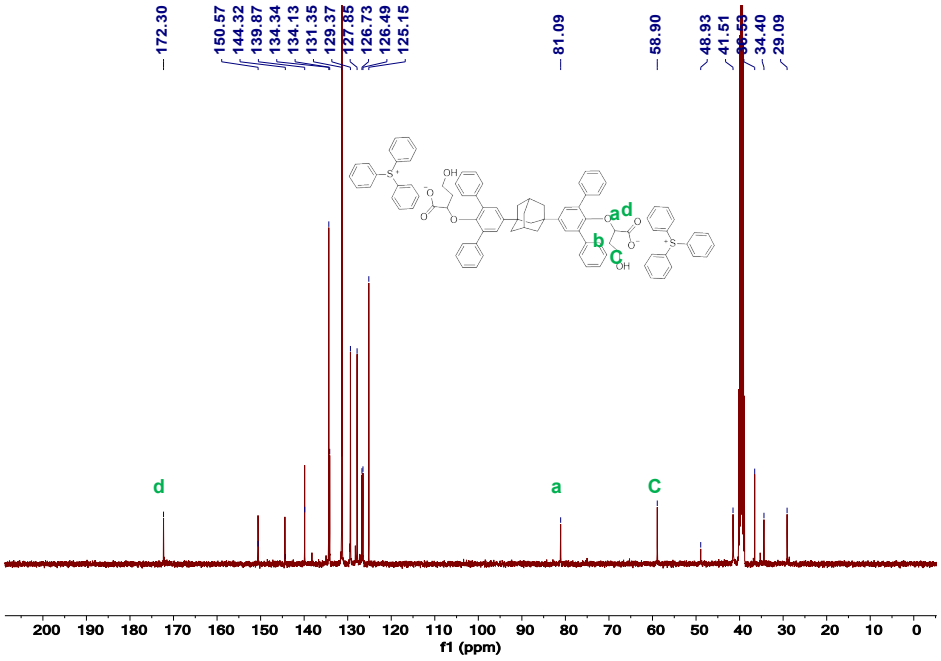

Figure S6. ^{13}C NMR spectrum of ADTPS. (DMSO-d_6, 151MHz).

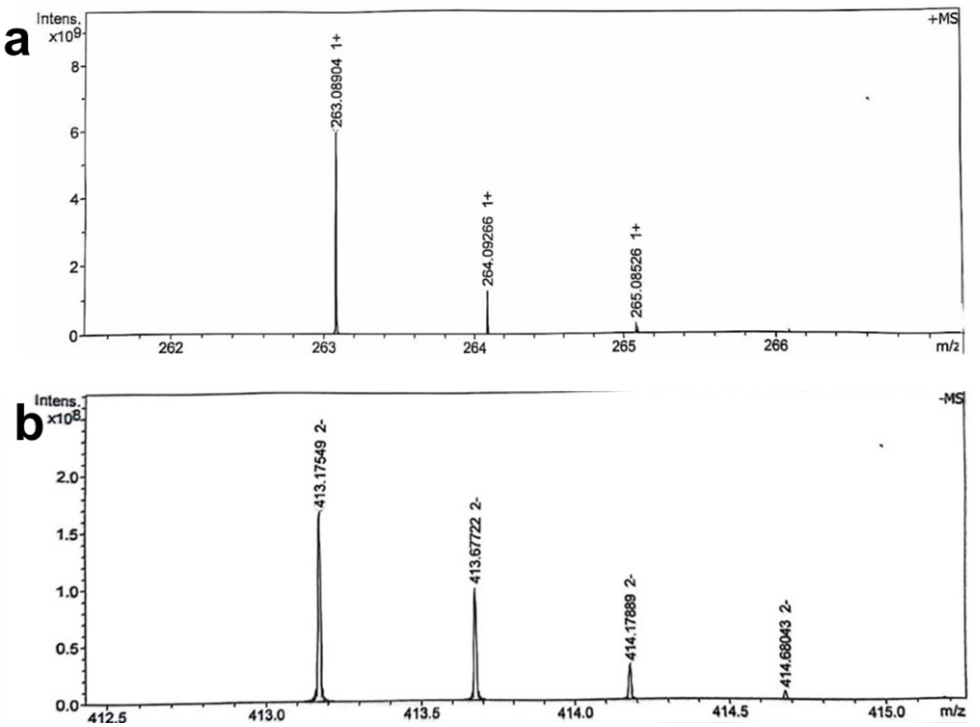

Figure S7. High-resolution ESI-TOF mass spectrum of ADTPS: a) positive; b) negative.

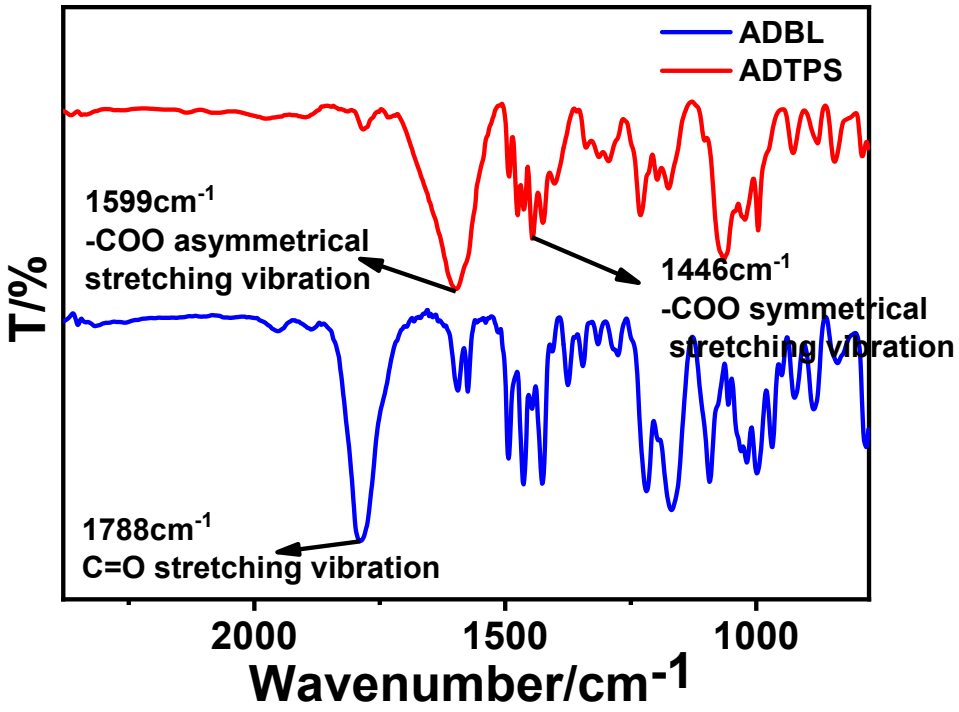

Figure S8. FTIR spectra of ADBL and ADTPS.

2. Normalized remaining thickness analysis

The contrast curves were obtained by fitting the film thickness data using a logistic function. According to the contrast curve, the tangent line at y=0.5 can be obtained. The dose of tangent at y =0 and 1 is considered as D_0 and D_{100}. The contrast could be calculated as

$$\gamma = \frac{1}{\left\{log\left(\frac{D_{100}}{D_0}\right)\right\}} \quad (1)$$

3. Lithographic performances of the ADTPS resist for PTD patterns by EBL

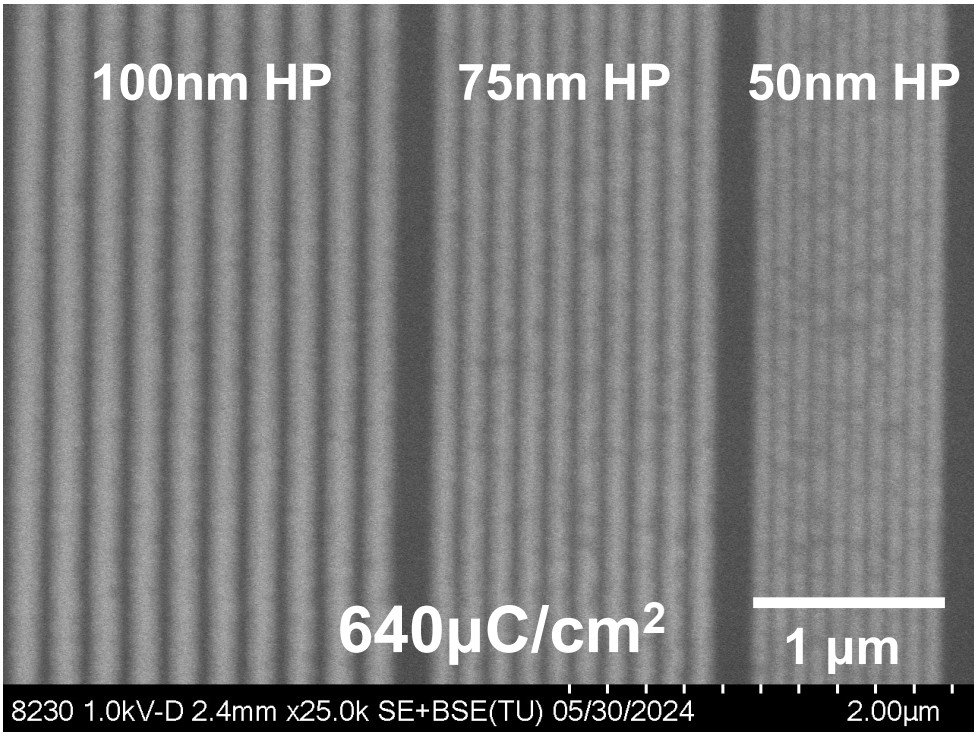

Figure S9. The SEM images of the 100, 75 and 50 nm L/S line PTD patterns of ADTPS resist exposed at 640 μC/cm^2 (Thickness: 40 nm; Developer: n-butyl acetate).

4. Lithographic performances of ADTPS resist by EUVL

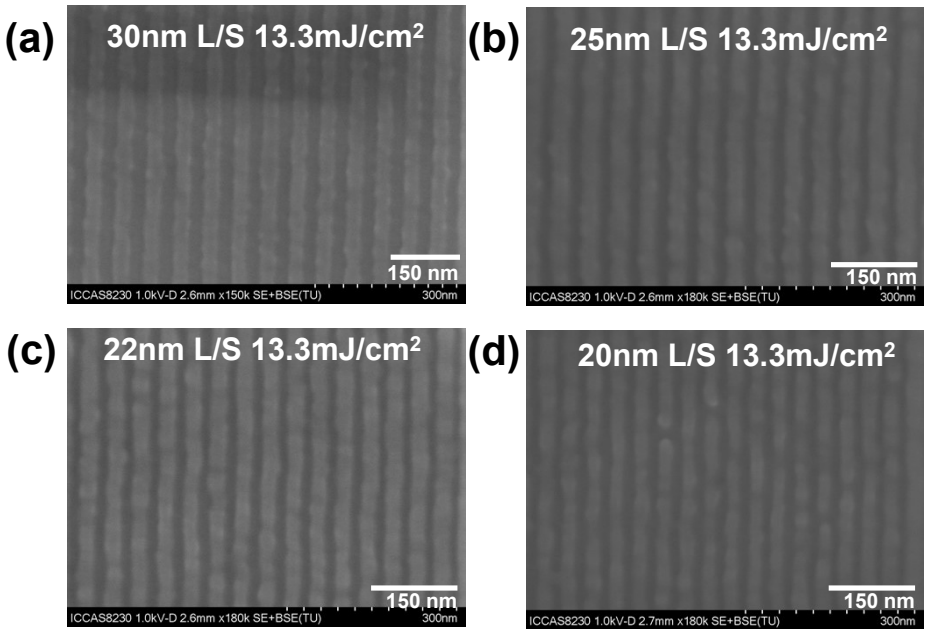

Figure S10. The SEM images of the 30, 25, 22, and 20 nm L/S line patterns of ADTPS resist exposed at 13.3 mJ/cm^2 (Thickness: 30 nm; Developer: water/ethanol = 2/1).

5. Lithographic performances of ADTPS resist by EUVL

Table S1. Summary of the performances of ADTPS resist and newly reported n-CARs.

Resist	Tone	LER(nm)	[a] Sensitivity [b] ($\mu C/cm^2$) [c] (mJ/cm^2)	Resolution (nm HP)	Ref
ADTPS	Negative	4.1	160[b1]	22	This work
ADTPS	Negative	5.0	13.3[c]	20	This work
$PSOS_{100}$	Negative	3.2	920[b1]	20	15
$PSOS_{100}$	Negative	2.3	87.1[c]	18	15
$[(BuSn)_{12}O_{14}(OH)_6](OH)_2$	Negative	-	29.5[c]	50	16
PLC_{44}	Negative	4.6	-[b1]	100	17
$PLDC_{47}$	Positive	26.7	-[b1]	100	17
$TPESF_6$	Negative	1.8	372.6[c]	13	18
Material 2	Positive	4.6	119[c]	30	23
$PSTS_{0.7}$	Negative	2.8	186[c]	13	25
$PS\text{-}I_{0.58}$	Negative	3.6	2000[b1]	15	27
PSNA0.4	Negative	4.0	1300[b1]	18	28
PSNA0.4	Negative	2.6	90.8[c]	22	28
MAPDST-co-ADSM (Sn:1.70wt%)	Negative	-	800[b2]	25	29
MAPDST-co-ADSM(Sn:2.48wt%)	Negative	-	350[b2]	25	29
$SnMSF_4$	Negative	-	2000[b1]	20	46
$SnMSF_4$	Negative	3.3	173[c]	13	46
$BPSS_4$	Negative	2.5	167[c]	13	47

[a] The sensitivity of EBL and EUVL is the optimal exposure dose for achieving the highest resolution patterning. [b1] Performance for EBL at an accelerating voltage of 100 keV. [b2] Performance for EBL at an accelerating voltage of 20 keV. [c] Performance for EUVL.

6. LER and LWR measurement of high-resolution SEM images

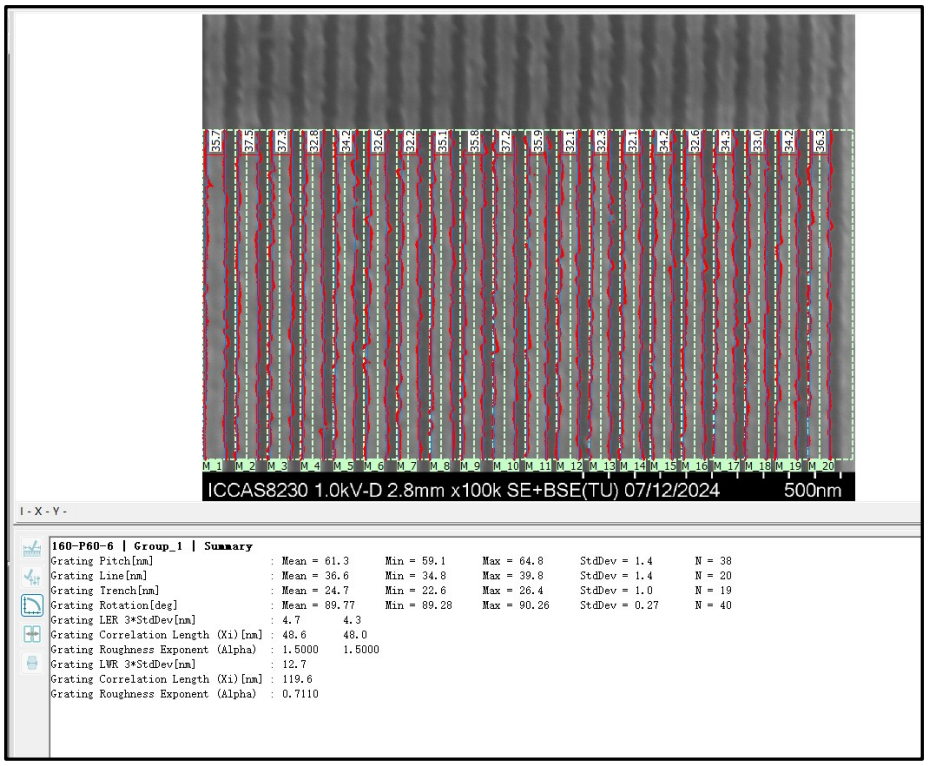

Figure S11. The LER and LWR measurement of ADTPS resist pattern (30 nm L/S) by EBL at 160 μC /cm^2.

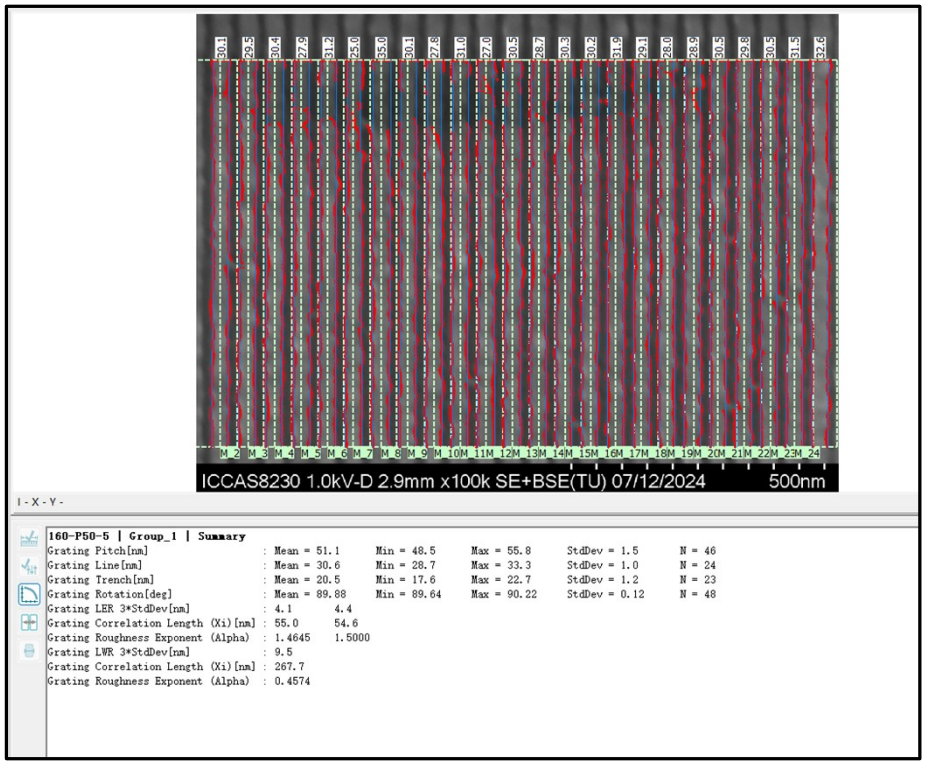

Figure S12. The LER and LWR measurement of ADTPS resist pattern (25 nm L/S) by EBL at 160 μC /cm^2.

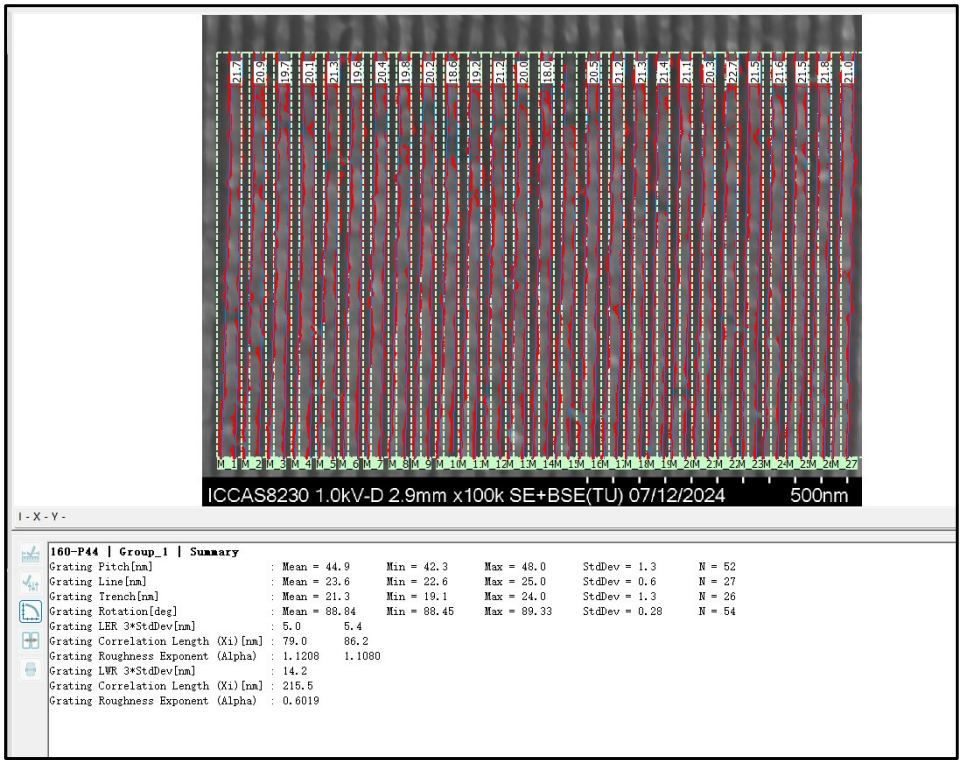

Figure S13. The LER and LWR measurement of ADTPS resist pattern (22 nm L/S) by EBL at 160 μC /cm^2

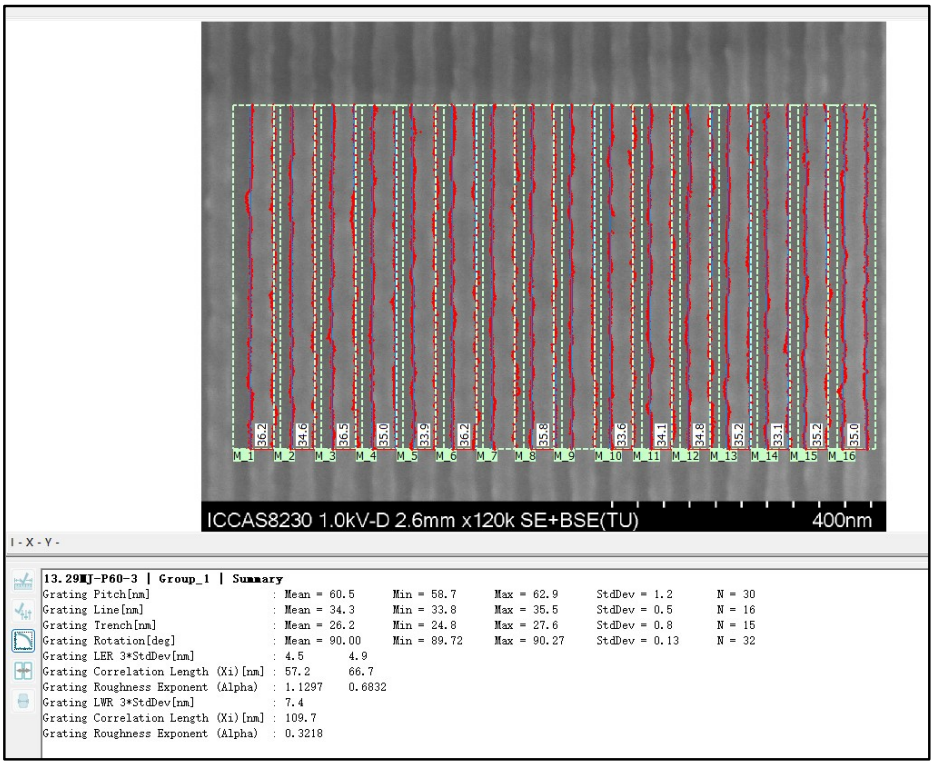

Figure S14. The LER and LWR measurement of ADTPS resist pattern (30 nm L/S) by EUVL at 13.3mJ /cm^2.

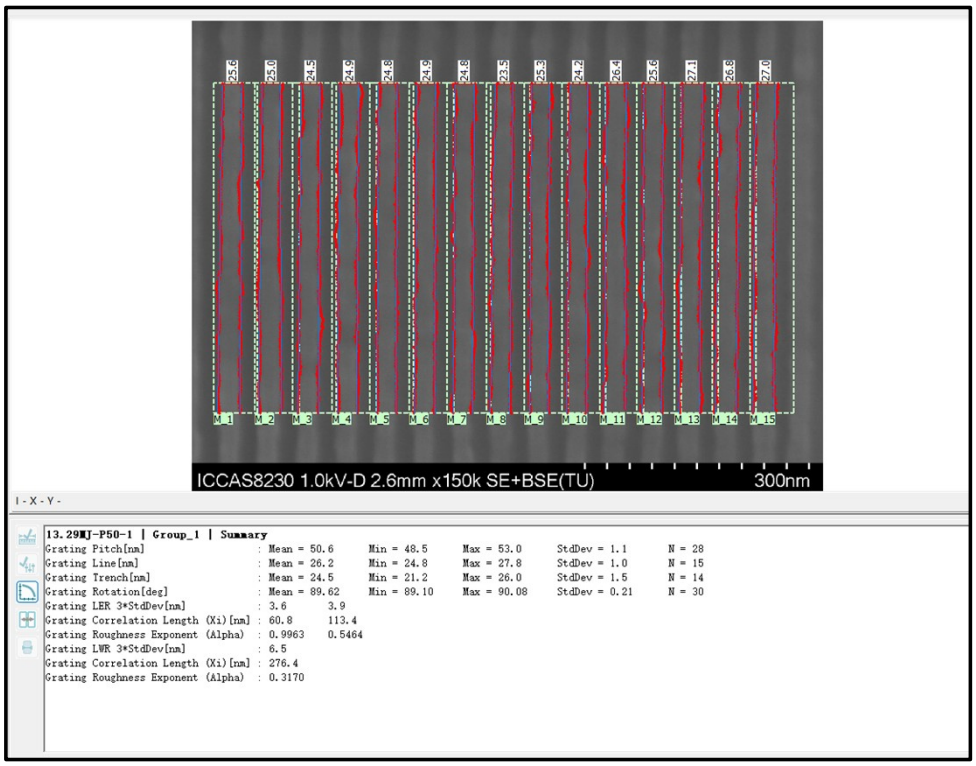

Figure S15. The LER and LWR measurement of ADTPS resist pattern (25 nm L/S) by EUVL at 13.3mJ /cm^2.

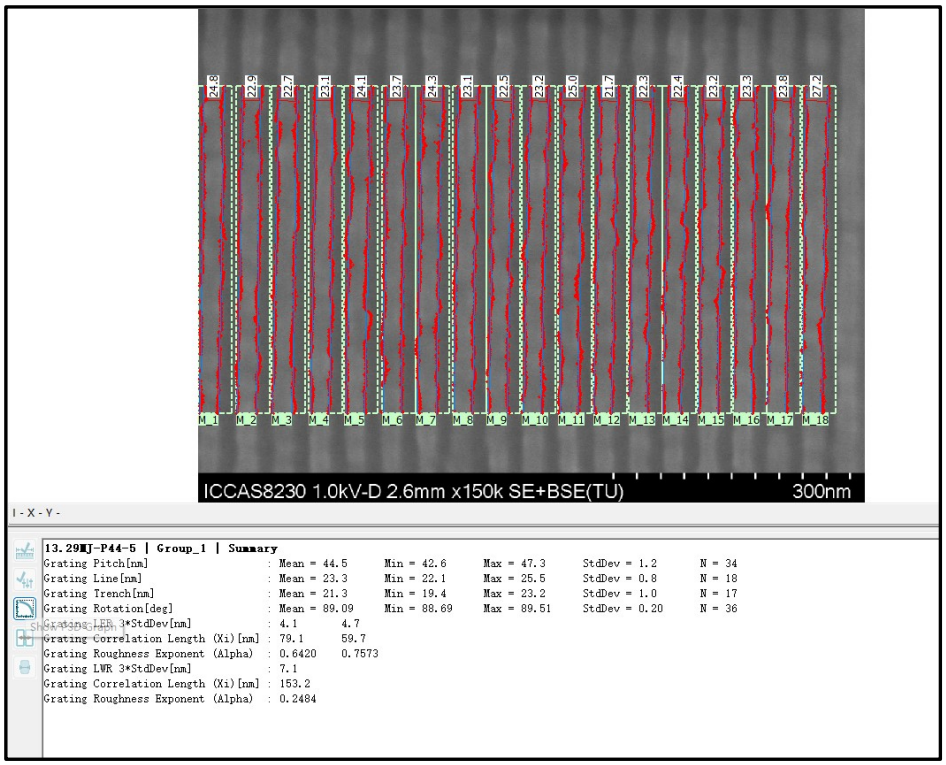

Figure S16. The LER and LWR measurement of ADTPS resist pattern (22 nm L/S) by EUVL at 13.3mJ /cm^2.

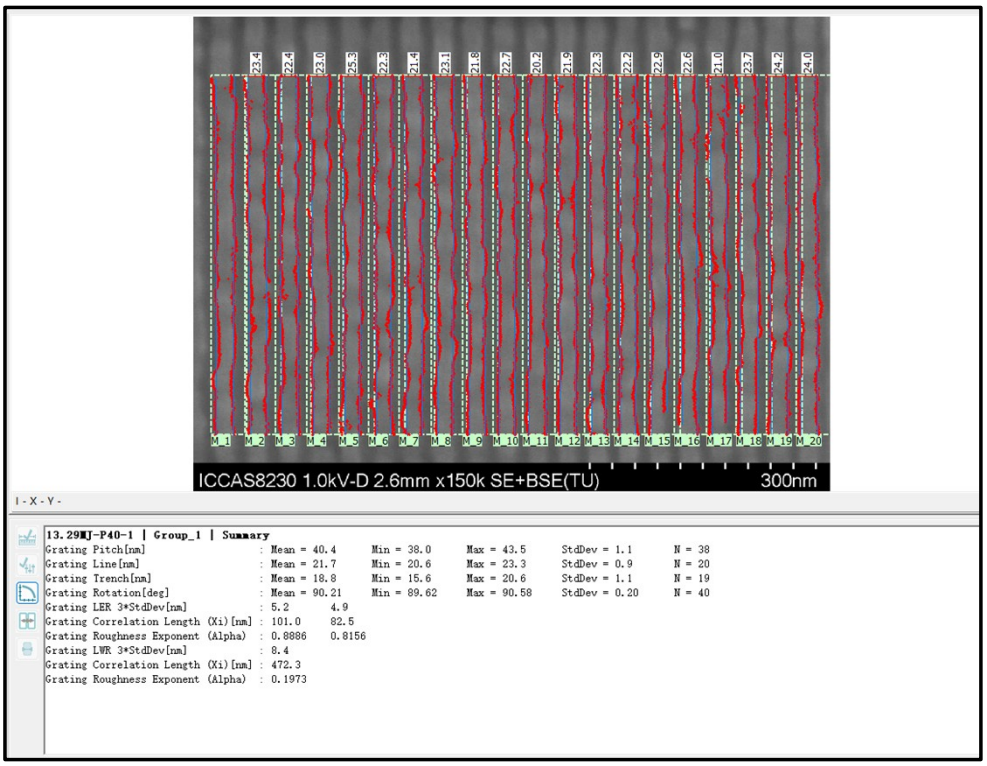

Figure S17. The LER and LWR measurement of ADTPS resist pattern (20 nm L/S) by EUVL at 13.3mJ /cm^2.

7. Mechanistic analysis of ADTPS resist pattern generation

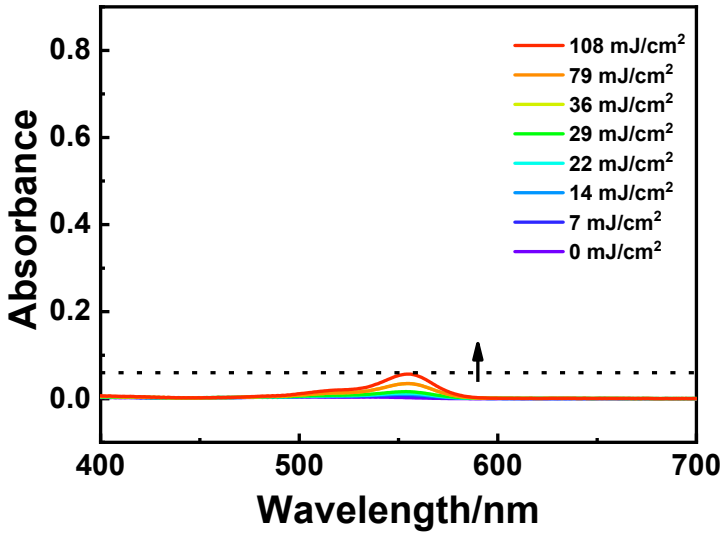

Figure S18. The UV absorbance of rhodamine B solution exposed to 254 nm light at different doses in acetonitrile.

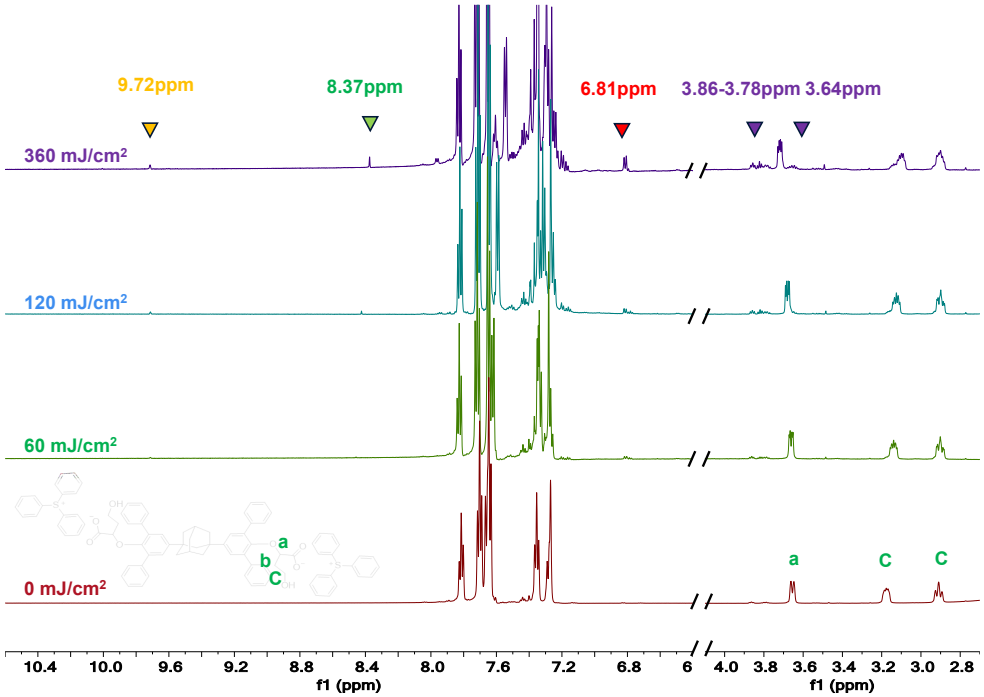

Figure S19. The ^{1}H NMR spectra of ADTPS in deuterated acetonitrile at different exposure doses of 254 nm light.