Supproting Information

An i-line molecular glass photoresist for high resolution patterning

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Experimental Section

Material

Resorcinol and paraldehyde were purchased from Aladdin Reagents Company (Shanghai, China). 2-diazo-1-naphthoquinone-4-sulfonyl chloride (2,1,4-DNQ-Cl) was purified by pouring the dioxane solution of 2,1,4-DNQ-Cl into excess ethanol. Triethylamine (TEA) was dried by refluxing with calcium chloride and redistilled before used. Other organic solvents were obtained from Beijing Chemical Reagents Company (AR, Beijing, China) and were used as received unless otherwise stated.

Equipment

FT-IR spectra were measured on Avatar 360 spectrometer (Nicolet, U.S.A.). The UV spectra were recorded on Cintra 10e UV-Visible spectrophotometer (GBC, Australia) by coating films on quartz plated. ^{1}H (400 MHz) and ^{13}C (100 MHz) nuclear magnetic resonance (NMR) spectra were measured on a Bruker Advance Ⅲ spectrometer in acetone-d_6 or dimethyl sulfoxide (DMSO-d_6). Elemental analyses were obtained by a

Vario El elemental analyzer (Elemental, Germany). The thermo gravimetric analysis (TGA) data were collected on a METTLER TOLEDO star system instrument with the heating rate of 10 °C min^{-1} under nitrogen ambient(20 mL min^{-1}). The glass transition temperature (T_g) of the MG compound was measured on a differential scanning calorimeter (DSC, METTLER STAR^e system) with a heating rate of 10 °C min^{-1} under nitrogen. Powder X-ray diffraction (PXRD) data were collected on a X' Pert PRO MPD diffractometer (PANalytical, Holand). The photoactive properties characterizations were evaluated by exposing the film to a 365 nm UV lamp (GY-13, Tianjin, China). The lithographic evaluation was performed on an Argon ion laser interference lithography equipment

Synthesis of C-methyl-calix[4]resorcinarene(C-4-R)

As shown in Scheme 1, resorcinol (49.5 g, 0.45 mol) was dissolved in 440 mL water and then cooled to 5 °C using ice bath. 110 mL concentrated hydrochloric acid was added to the solution under stirring over 0.5 h. After stirring for another 10 minutes, paraldehyde (20 mL, 0.15 mol) was added dropwise into the solution over 0.5 h. The reaction solution was refluxed at 75 °C for 6 h. After being cooled to room temperature, the yellow precipitate was collected and washed two times with water. The resulting product was then recrystallized from methanol and dried at 60 °C overnight under reduced pressure. Yield: 40 g (65.3%). IR (KBr, cm^{-1}): 3395 (-OH). ^{1}H-NMR (acetone-d_6): δ (ppm) 1.76 (d, CH_3, 12H), 4.52 (q, CH, 4H), 6.22 (s, ArH, 4H), 7.65 (s, ArH, 4H), 8.48 (s, OH, 8H); ^{13}C-NMR (DMSO-d_6): δ (ppm) 20.3 (CH_3), 28.7 (CH), 103.6 (ArC),125.2, 126.1, 152.3. Anal. Calcd for $C_{32}H_{32}O_8$: C, 70.60; H, 5.88. Found: C, 67.3,H, 6.38.

Synthesis of DNQ functionalized calix[4]resorcinarene(DNQ-C-4-R)

To the solution of C-4-R (5.44 g, 10 mmol) in 150 mL mixed solvents (acetone:DMF=1:2), triethylamine (5.82mL, 40mmol) was added dropwise with vigorous stirring under an N_2 atmosphere. 214-DNQ-Cl(10.74g, 40mmol) was dissolved in further 50 mL solvent and added dropwise to the flask. After stirring at room temperature for 24 h, the contents of the flask was poured tinto a 10-fold excess of distilled water. The resulting precipitate was collected and washed with water, and then dried overnight at 50 °C. This basic procedure was repeated with the variation in the molar quantities of 214-DNQ-Cl and triethylamine to produce different degree of functionalized compound.

1a(average functionalization ratio 32.5%). Yield: 94%. ^{1}H-NMR (DMSO-d_6): δ(ppm) 1.2-1.3(CH_3, 12H), 4.3-4.4(CH, 1H), 6.0-8.6(unsaturated proton, 6H)。Anal.Calcd. for $C_{62}H_{44}O_{17}N_6S_3$, C: 60.01; H: 3.54; N: 6.77. Found, C: 58.21; H: 3.87;N: 6.92.

1b(average functionalization ratio 50%). Yield: 91%. ^{1}H-NMR (DMSO-d_6): δ(ppm) 1.2-1.3(CH_3, 12H), 4.3-4.4(CH, 1H), 5.9-8.6(unsaturated proton, 7.5H)。Anal.Calcd. for $C_{72}H_{48}O_{20}N_8S_4$, C: 58.69; H: 3.26; N: 7.61. Found, C:56.76; H: 3.73; N: 7.87.

1c(average functionalization ratio 62.5%). Yield：84%. ^{1}H-NMR (DMSO-d_6): δ(ppm) 1.2-1.3(CH_3, 12H), 4.3-4.4(CH, 1H), 5.9-8.6(unsaturated proton, 8.7H)。Anal.Calcd. for $C_{82}H_{52}O_{23}N_{10}S_5$, C: 57.74; H: 3.05; N: 8.21. Found, C: 55.85; H: 3.45; N: 8.32.

Solubility of DNQ-C-4-R

Table 1. The solubility of compound 1a-1c in various solvents [a]

Solvents [polarity index]	1a	1b	1c
Water[10.2]	-	-	-
DMSO[7.2]	++	++	++
DMAc[6.5]	++	++	++
DMF[6.4]	++	++	++
Acetonitrile[6.2]	-	-	-
Methanol[6.6]	-	-	-
Acetone[5.4]	-	-	-
1,4-dioxine[4.8]	++	++	++
2-Butanone [4.5]	-	-	-
Ethyl acetate [4.3]	-	-	-
Chloroform [4.4]	-	-	-
THF[4.2]	++	++	++
2-Propanol [4.2]	-	-	-
Toluene [2.4]	-	-	-
Cyclohexane [0.1]	-	-	-
PGMEA[b]	++	+	+
Cyclohexanone[b]	++	++	+
Ethylene glycol monoethyl ether[b]	++	++	++
Butyl acetate[b]	-	-	-
Ethyl lactate[b]	++	++	++

[a] -: insoluble, +: partially soluble, ++: soluble at room temperature

[b] the commonly used photoresist solvents