Supporting Information

Ambient condition and oxygen-tolerant photopolymerization from near-UV to blue light *via* naphthimide-borate synergy

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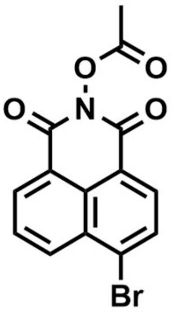
1. Additional Experimental Section

1.1 Synthesis of photoinitiators

6-bromo-1,3-dioxo-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl acetate (**NAc**)



Chemical Formula: $C_{14}H_8NO_4$

Molecular Weight: 334.1250

6-Bromo-1*H*,3*H*-benzo[*de*]isochromene-1,3-dione (11.0829 g, 40 mmol), hydroxylamine hydrochloride (5.5592 g, 80 mmol), and sodium acetate (6.5628 g, 80 mmol) were added in a mixture of methanol: tetrahydrofuran: water (200/40/40, v/v/v), and the solution was refluxed for 8 h. After cooling, the organic solvent was removed under reduced pressure. The residue was washed several times with deionized water and freeze-dried for 48 h. The crude product of 6-bromo-2-hydroxy-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione was obtained (NH, 99% yield).

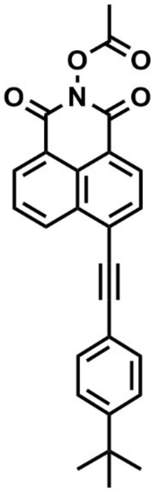
The crude product of NH (5.8418 g, 20 mmol) obtained above and dry triethylamine (2.5298 g, 25 mmol) were dissolved in 120 mL of ultra-dry dichloromethane. Then, acetyl chloride (1.9624 g, 25 mmol) was added under an ice bath. The reaction flask was then stirred at room temperature overnight. The solution was subsequently washed with sodium bicarbonate and ammonium chloride aqueous solutions and dried over anhydrous sodium sulfate. After solvent removal, the obtained powder was sequentially washed with ethanol, filtered, vacuum-dried, and then directly subjected to the next reaction. The product was further purified using flash column chromatography (silica gel, dichloromethane/petroleum ether, 2:1, v/v). (NAc, 86% yield)

^{1}H NMR (400 MHz, chloroform-*d*): δ 8.71 - 8.61 (m, 2H), 8.44 (d, J = 7.9 Hz, 1H), 8.08 (d, J = 7.9 Hz, 1H), 7.88 (dd, J = 8.6, 7.3 Hz, 1H), 2.47 (s, 3H).

HRMS (ESI MS) m/z

Theor: 332.9637, found (M + H^+. detected): 333.9703.

6-((4-(*tert*-butyl)phenyl)ethynyl)-1,3-dioxo-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl acetate (**NE1**)



Chemical Formula: $C_{26}H_{21}NO_4$

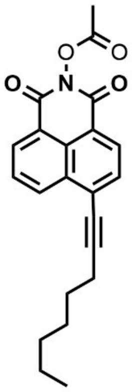
Molecular Weight: 411.4570

6-Bromo-1,3-dioxo-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl acetate (2.3389 g, 7.00 mmol), triphenylphosphine (TPP, 0.1469 g, 0.56 mmol), and dichlorobis(triphenylphosphine)palladium(II) ($Pd(PPh_3)_2Cl_2$, 0.2456 g, 0.35 mmol) were added in a 100 mL flask-3-neck. The mixed solutions were placed in a nitrogen atmosphere, and tetrahydrofuran (THF, molecular sieve drying for 48 h) was added and stirred at room temperature. Then, diisopropylamine (DIPA, 2.8333 g, 28.00 mmol) and 4-*tert*-butylphenylacetylene (1.2185 g, 7.70 mmol) were added. After nitrogen blowing for 60 min, a tetrahydrofuran solution of pre-deoxidized cuprous iodide (0.0240 g) was added *via* syringe and reacted at 55 °C for 6 h. After completion of the reaction, the insoluble materials were removed by filtration. The organic products were extracted with dichloromethane, and the organic phase was washed sequentially with aqueous sodium bicarbonate and ammonium chloride solutions. The organic layer was then dried over anhydrous sodium sulfate. After solvent removal, the crude product was triturated with a dichloromethane/petroleum ether mixture and filtered to afford the product as a powder. Further purification was achieved by column chromatography (silica gel, chloroform/petroleum ether, 10:6 to 10:1, v/v) or recrystallization (dichloromethane/ethanol/petroleum ether, 10:3:5, v/v/v). (NE1, 84% yield)

^{1}H NMR (400 MHz, chloroform-*d*): δ 8.79 (dd, J = 8.3, 1.2 Hz, 1H), 8.65 (dd, J = 7.3, 1.2 Hz, 1H), 8.57 (d, J = 7.6 Hz, 1H), 7.95 (d, J = 7.7 Hz, 1H), 7.85 (dd, J = 8.4, 7.3 Hz, 1H), 7.64 - 7.59 (m, 2H), 7.51 - 7.43 (m, 2H), 2.48 (s, 3H), 1.36 (s, 9H).

HRMS (ESI MS) m/z
Theor: 411.1471, found (M + H^+. detected): 412.1503.

Synthesis of 6-(oct-1-yn-1-yl)-1,3-dioxo-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl acetate (**NE2**)



Chemical Formula: $C_{22}H_{21}NO_4$

Molecular Weight: 363.4130

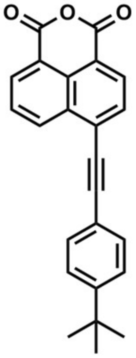
6-Bromo-1,3-dioxo-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl acetate (2.0047 g, 6.00 mmol), triphenylphosphine (0.1259 g, 0.48 mmol), and dichlorobis(triphenyl-phosphine)palladium(II) (0.2105 g, 0.30 mmol) were added in a 100 mL flask-3-neck. The mixed solutions were placed in a nitrogen atmosphere, and tetrahydrofuran was added and stirred at room temperature. Then, diisopropylamine (2.4285 g, 24.00 mmol) and 1-octyne (0.7494 g, 6.80 mmol) were added. After nitrogen blowing for 60 min, a tetrahydrofuran solution of pre-deoxidized cuprous iodide (0.0205 g) was added *via* syringe and reacted at 55 °C for 6 h. Upon completion of the reaction, insoluble materials were removed by filtration. The organic products were extracted with dichloromethane, washed sequentially with sodium bicarbonate and ammonium chloride aqueous solutions, and dried over anhydrous sodium sulfate. After solvent removal, the crude product was triturated with a dichloromethane/petroleum ether mixture and filtered to afford the product as a powder. Further purification was achieved by column chromatography (silica gel, chloroform/petroleum ether, 1:1 to 4:1, v/v). (NE2, 80% yield).

^{1}H NMR (400 MHz, chloroform-*d*): δ 8.69 (dd, J = 8.4, 1.2 Hz, 1H), 8.63 (dd, J = 7.3, 1.2 Hz, 1H), 8.52 (d, J = 7.6 Hz, 1H), 7.85 - 7.77 (m, 2H), 2.62 (t, J = 7.1 Hz, 2H), 2.47 (s, 3H), 1.74 (p, J = 7.2 Hz, 2H), 1.58 - 1.50 (m, 2H), 1.37 (h, J = 3.8 Hz, 4H), 0.97 - 0.90 (m, 3H).

HRMS (ESI MS) m/z

Theor: 363.1471, found (M + Na$^+$. detected): 386.1358.

Synthesis of 6-((4-(*tert*-butyl)phenyl)ethynyl)-1*H*,3*H*-benzo[*de*]isochromene-1,3-dione (**NO**)



Chemical Formula: $C_{24}H_{18}O_3$

Molecular Weight: 354.4050

6-Bromo-1*H*,3*H*-benzo[*de*]isochromene-1,3-dione (0.5541 g, 2.00 mmol), triphenylphosphine (TPP, 0.0420 g, 0.16 mmol), and dichlorobis(triphenylphosphine)palladium(II) ($Pd(PPh_3)_2Cl_2$, 0.7010 g, 0.10 mmol) were added in a 50 mL flask-3-neck. The mixed solutions were placed in a nitrogen atmosphere, and tetrahydrofuran (THF, molecular sieve drying for 48 h) was added and stirred at room temperature. Then, diisopropylamine (DIPA, 0.8095 g, 8.00 mmol) and 4-*tert*-butylphenylacetylene (0.3323 g, 2.1 mmol) were added. After nitrogen blowing for 60 min, a tetrahydrofuran solution of pre-deoxidized cuprous iodide (0.0150 g) was added *via* syringe and reacted at 55 °C for 6 h. After completion of the reaction, the insoluble materials were removed by filtration. The organic products were extracted with dichloromethane, and the organic phase was washed sequentially with aqueous sodium bicarbonate and ammonium chloride solutions. The organic layer was then dried over anhydrous sodium sulfate. Further purification was achieved by column chromatography (silica gel, dichloromethane/petroleum ether, 1.5:1, v/v). (NO, 71% yield)

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.82 (dd, J = 8.4, 1.2 Hz, 1H), 8.66 (dd, J = 7.3, 1.2 Hz, 1H), 8.57 (d, J = 7.6 Hz, 1H), 7.98 (d, J = 7.6 Hz, 1H), 7.89 (dd, J = 8.4, 7.3 Hz, 1H), 7.64 – 7.58 (m, 2H), 7.51 – 7.44 (m, 2H), 1.37 (s, 9H).

HRMS (ESI MS) m/z

Theor: 354.1256, found (M + H^+. detected): 355.1325.

1.2 Device characterization

Photopolymerization experiments

The photopolymerization system consisted of a *tert*-butyl acrylate/*N*,*N*-dimethylformamide mixture (1:4, wt/wt), with the photoinitiator (NE1, NE2, or TPO) added at a concentration of 0.7 wt.% relative to the total mixture. Photopolymerization was carried out under 405 nm LED irradiation (25 mW/cm^2) for 5 h. Before irradiation, nitrogen was purged through the glass vials for 20 min to eliminate dissolved oxygen. The monomer conversion rate (C%) of NEs-initiated acrylic resins was tested by gel permeation chromatography (GPC, Waters, USA) according to equation (1) using tetrahydrofuran as a mobile phase, and the number-average molecular weight (M_n) was determined using polystyrene standards.

$$C\% = (A_0 - A)/A_0 \times 100\% \tag{1}$$

where A_0 is the peak area corresponding to *tert*-butyl acrylate before irradiation and A represents the peak area corresponding to *tert*-butyl acrylate after irradiation.

Cyclic Voltammetry

All electrochemical experiments were performed on a CHI660E Electrochemical Workstation (Shanghai Chenhua Instrument Corporation, China). The working electrode was a 3 mm diameter platinum disk, polished and cleaned with 0.05 µm alumina powder before testing. All potentials were measured on Ag/AgCl electrodes. A platinum wire was used as an auxiliary electrode. The working concentration of NEs was 1.6×10^{-3} M. The supporting electrolyte was an ultra-dry methylene chloride solution of 0.1 M tetrabutylammonium hexafluorophosphate. Argon was used to remove oxygen before testing, and an argon atmosphere was maintained during testing. The Gibbs free energy (ΔG) for an electron transfer reaction was calculated using the Rehm-Weller equation corresponding to equation (2).[1]

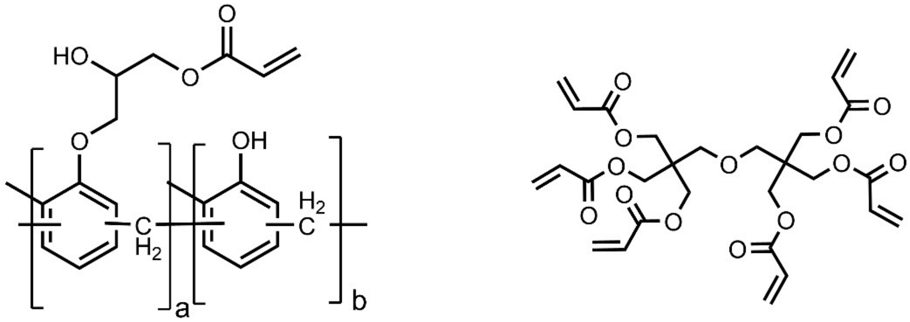
$$\Delta G = E_{ox} - E_{red} - E_{S1} + C \tag{2}$$

where E_{ox}, E_{red}, E_{S1}, and C are the oxidation potential (half-wave potential) of the electron donor (PhB), the reduction potential (half-wave potential) of the electron acceptor (NE), the excited state energy, and the coulombic term for the initially formed ion pair, respectively. Here, C is neglected for polar solvents.

Other characterizations

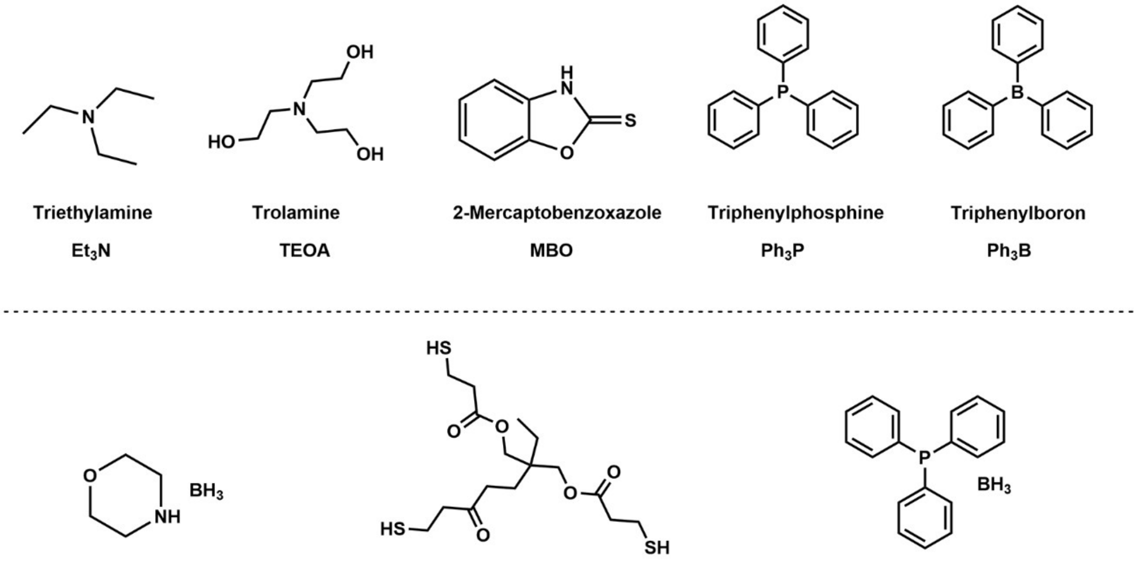
Proton nuclear magnetic resonance (^{1}H NMR) spectra of photoinitiators were recorded in a Bruker Avance III HD 400 MHz spectrometer, using chloroform-*d* as the solvent. High-resolution mass spectrometry (HRMS) measurements were performed using a Bruker Impact II mass spectrometer. The purity of NE1 was analyzed by liquid chromatography using a Leaps high-performance liquid chromatography (HPLC) system (Chromai). The analysis was conducted with a mobile phase consisting of acetonitrile and water (85:15, v/v), a flow rate of 1.0 mL/min, and a detection wavelength of 254 nm. Thermogravimetric analysis (Mettler Toledo, TGA-1) was conducted using a Mettler Toledo TGA-1 instrument under a nitrogen atmosphere. Fluorescence (FL) spectra were recorded using a FluoroMax-4 spectrofluorometer (Horiba). The photoinitiators were dissolved in ethyl acetate at a concentration of 5×10^{-5} mol/L. Optical microscope images of the photoresist patterns were taken using an LWT300LPT optical microscope (CEWEI).

2. Supporting Schemes



CCR-4959HW **DPHA**

Scheme S1. Chemical structures of the monomers of light-curing resins.



Triethylamine
Et_3N

Trolamine
TEOA

2-Mercaptobenzoxazole
MBO

Triphenylphosphine
Ph_3P

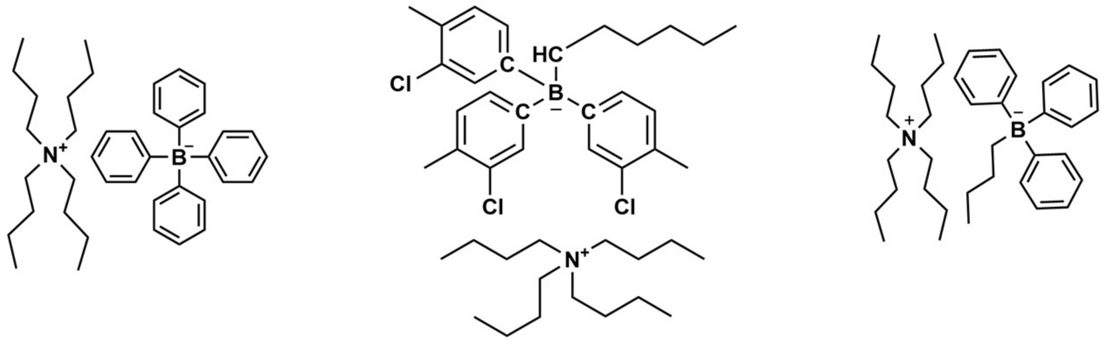
Triphenylboron
Ph_3B

Borane morpholine complex
BM

Trimethylolpropane-tris(3-mercaptopropionate)
TMPMP

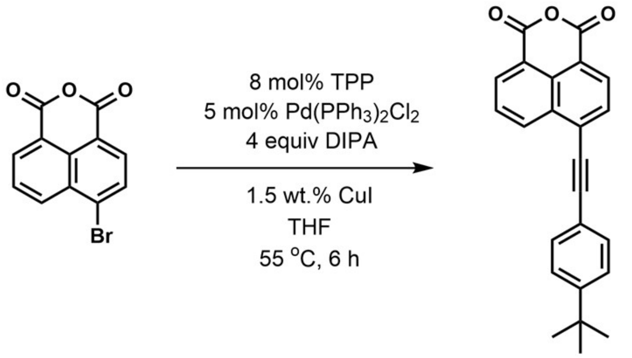
Borane triphenylphosphine complex
Ph_3PB

Scheme S2. Chemical structures of the additives.



TBATPB **TCTA** **PhB**

Scheme S3. Chemical structures of the borates.



71% yield

NO

Scheme S4. Synthetic routes of NO.

3. Supporting Figures

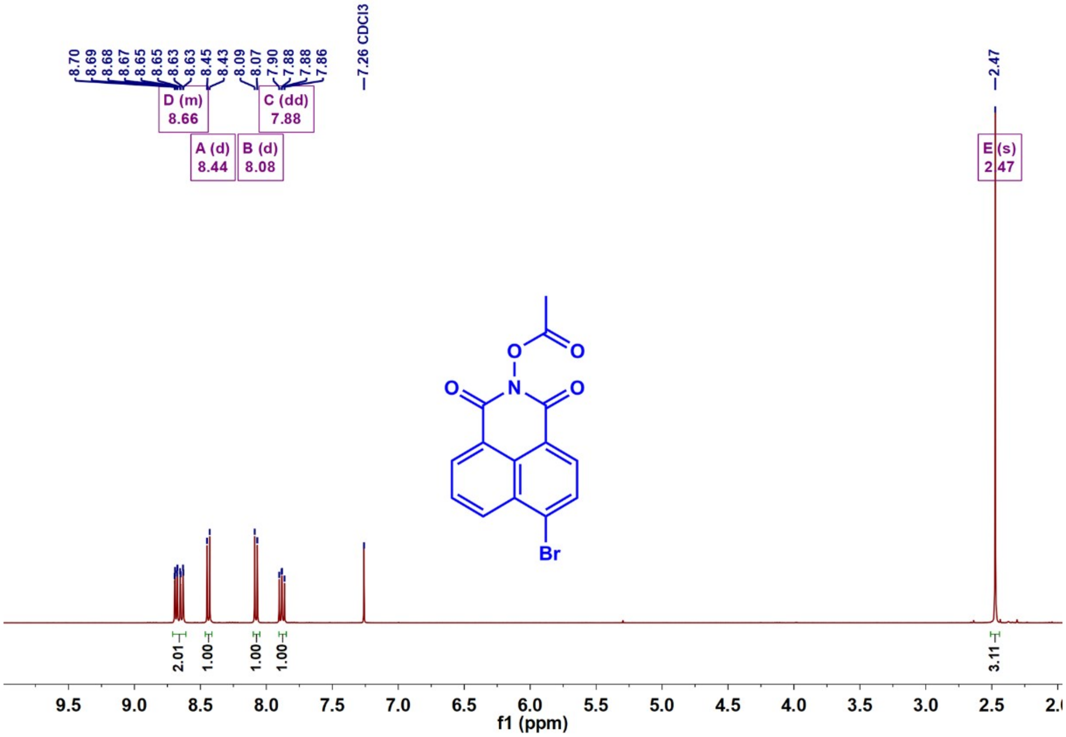


Figure S1. ^{1}H NMR spectrum of NAc.

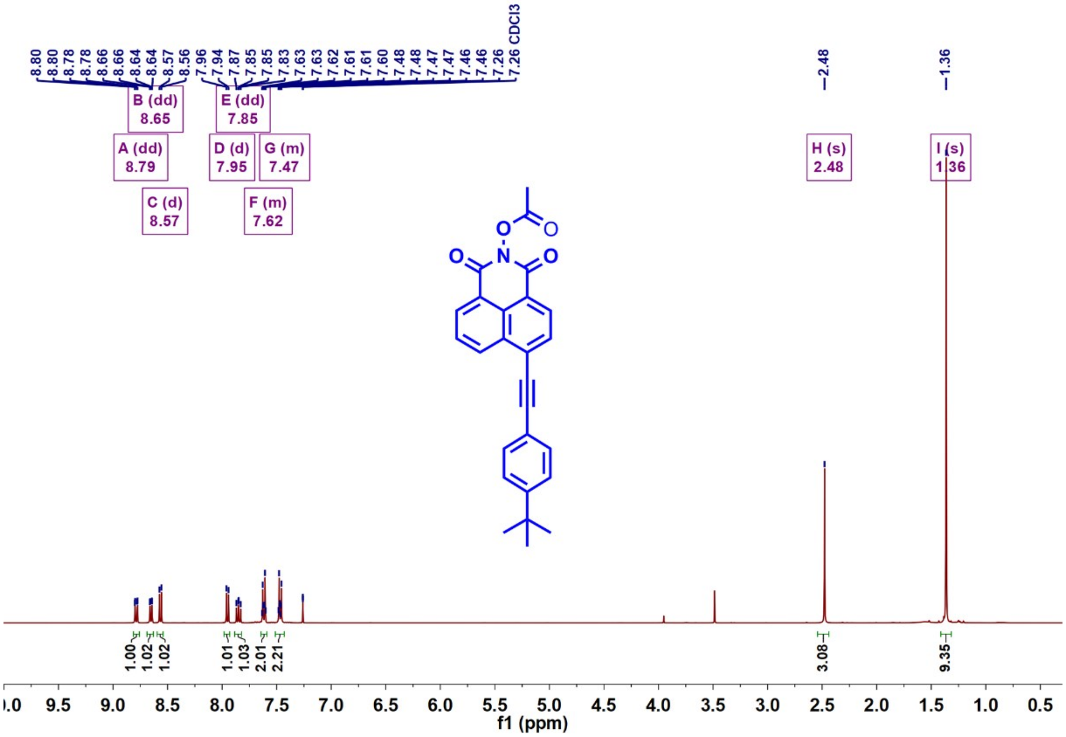


Figure S2. ^{1}H NMR spectrum of NE1 purified by column chromatography.

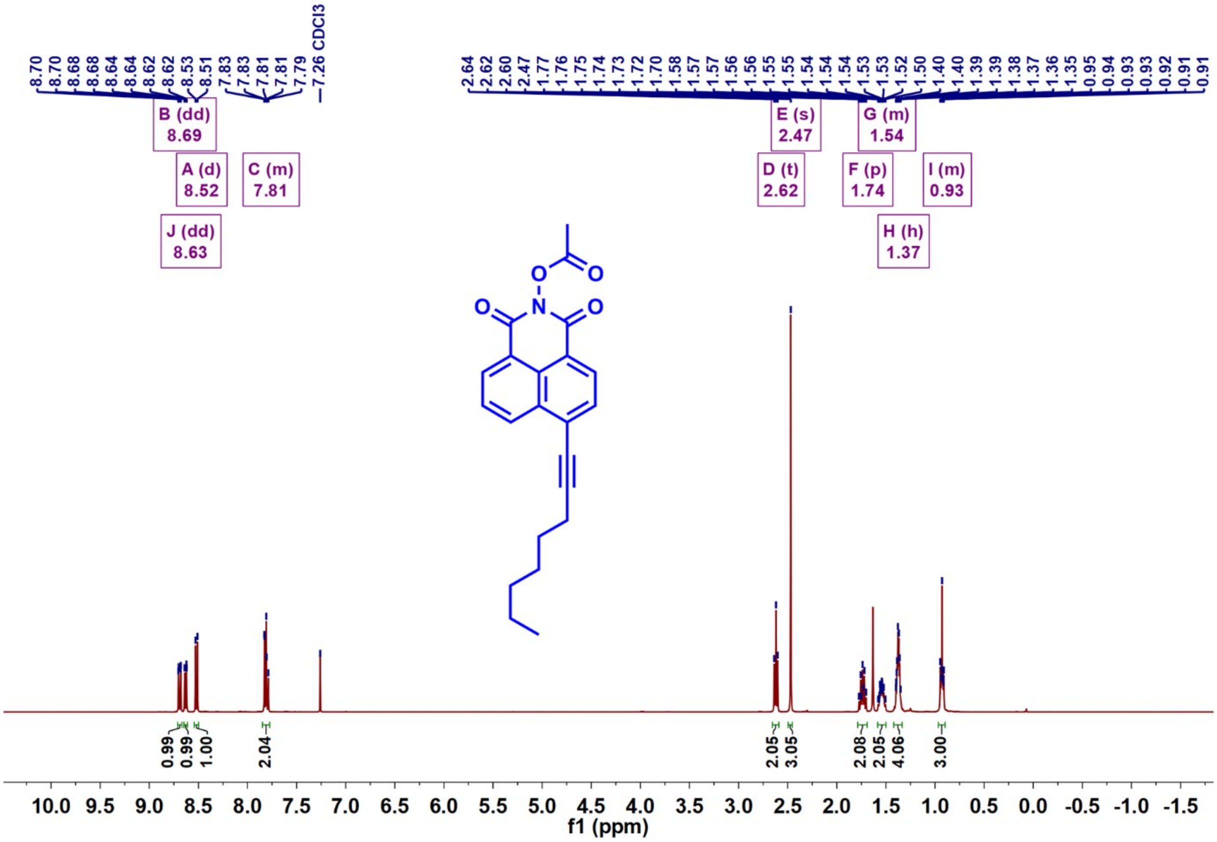


Figure S3. ^{1}H NMR spectrum of NE2.

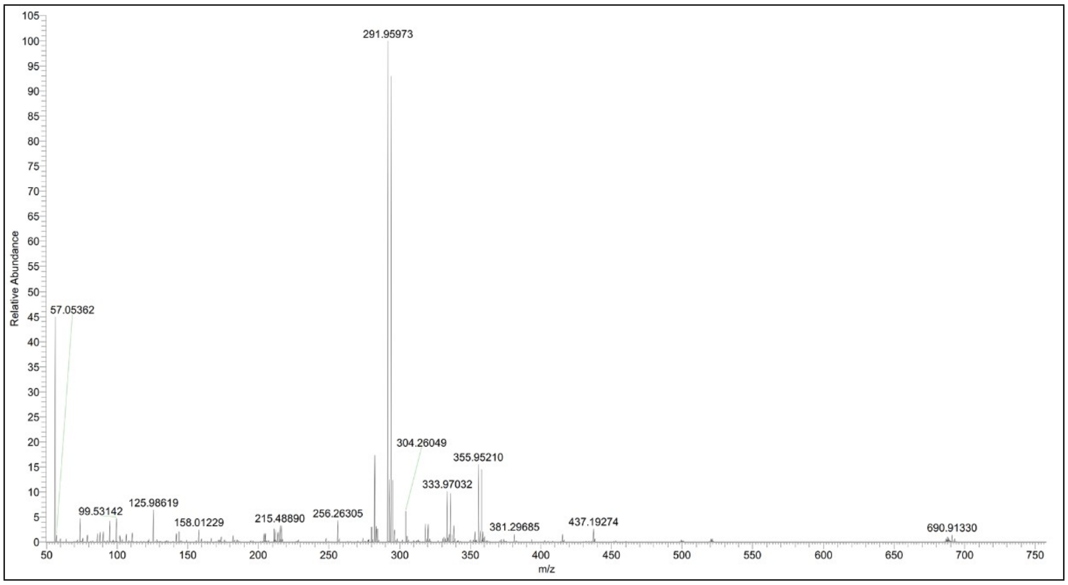


Figure S4. High-resolution mass spectrum of NAc. Theor: 332.9637, found (M + H$^+$. detected): 333.9703.

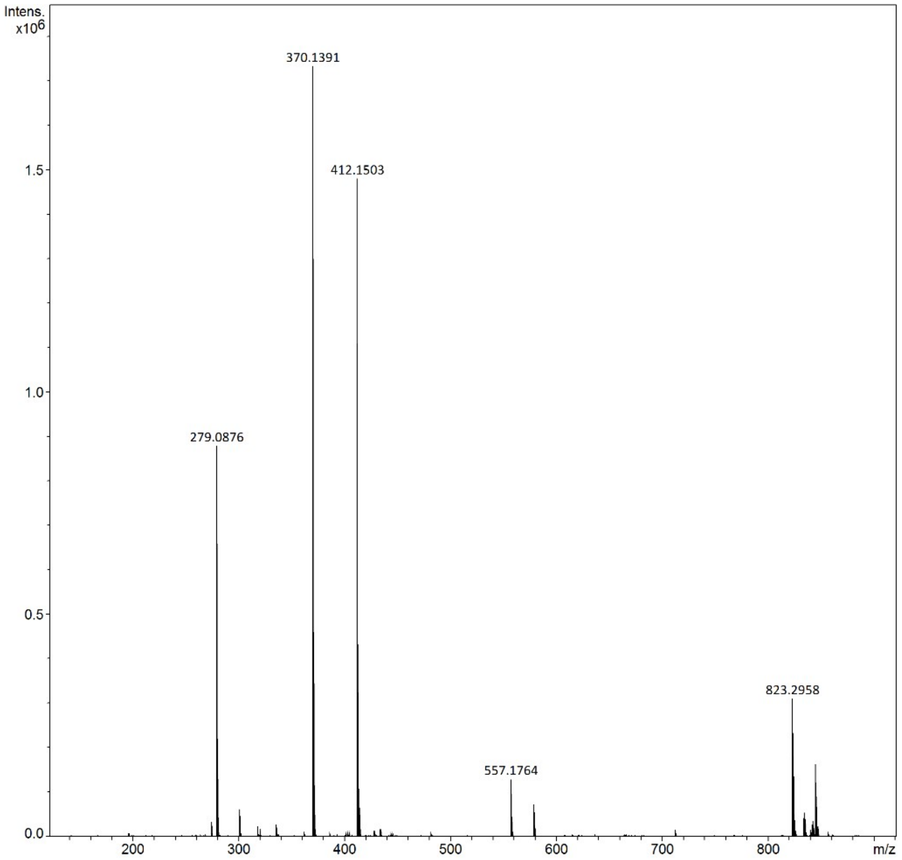


Figure S5. High-resolution mass spectrum of NE1 purified by column chromatography. Theor: 411.1471, found (M + H^+. detected): 412.1503.

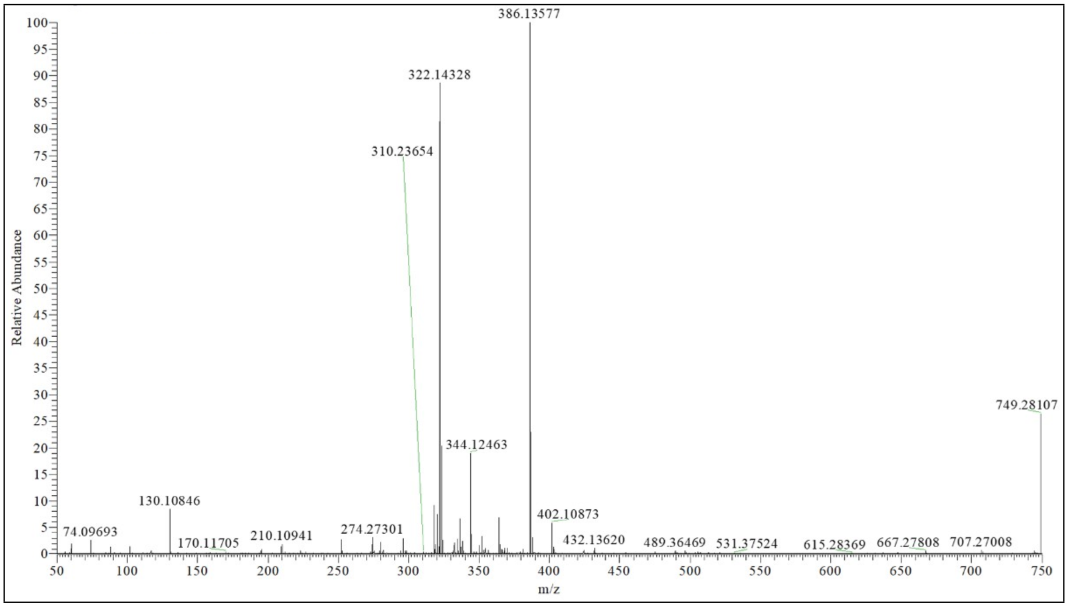


Figure S6. High-resolution mass spectrum of NE2. Theor: 363.1471, found (M + Na$^+$. detected): 386.1358.

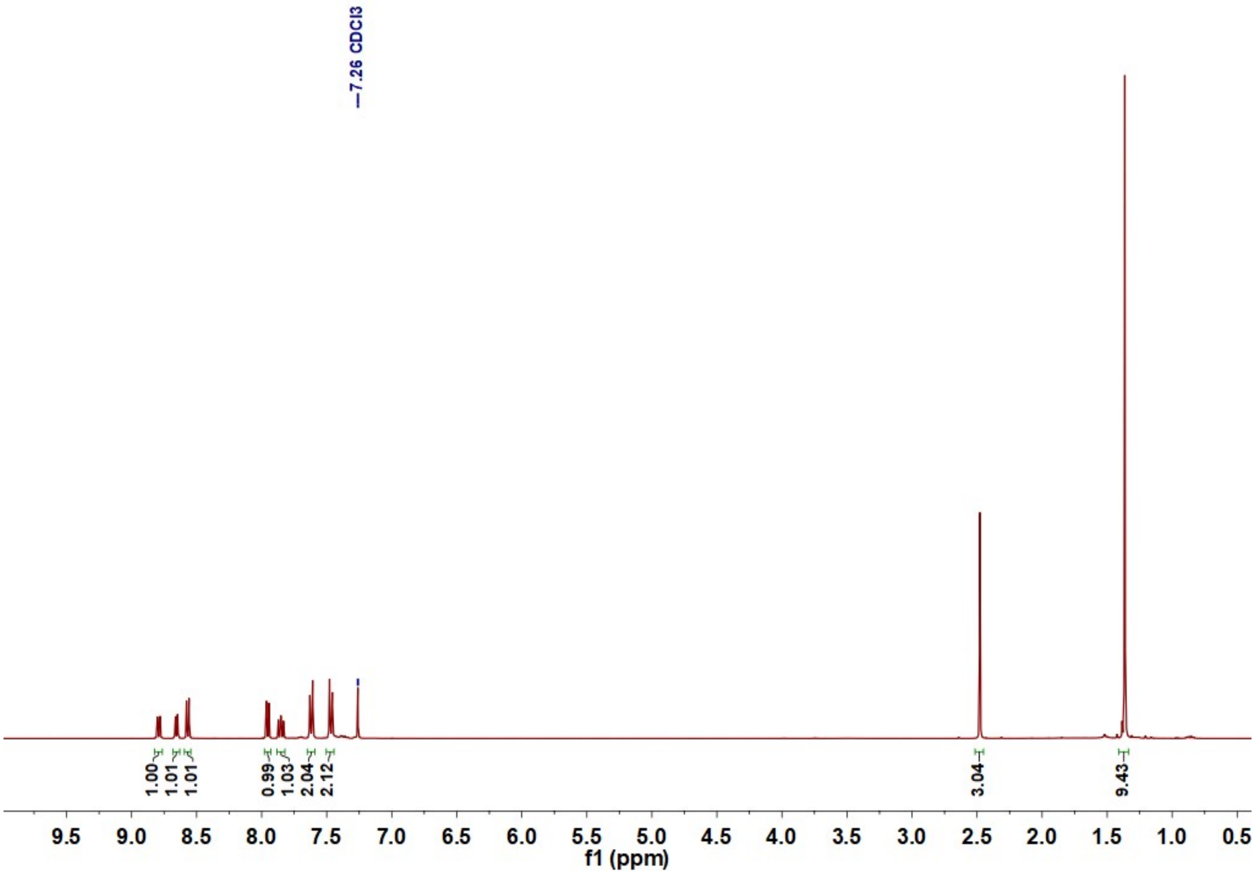


Figure S7. ^{1}H NMR spectrum of NE1 purified by recrystallization.

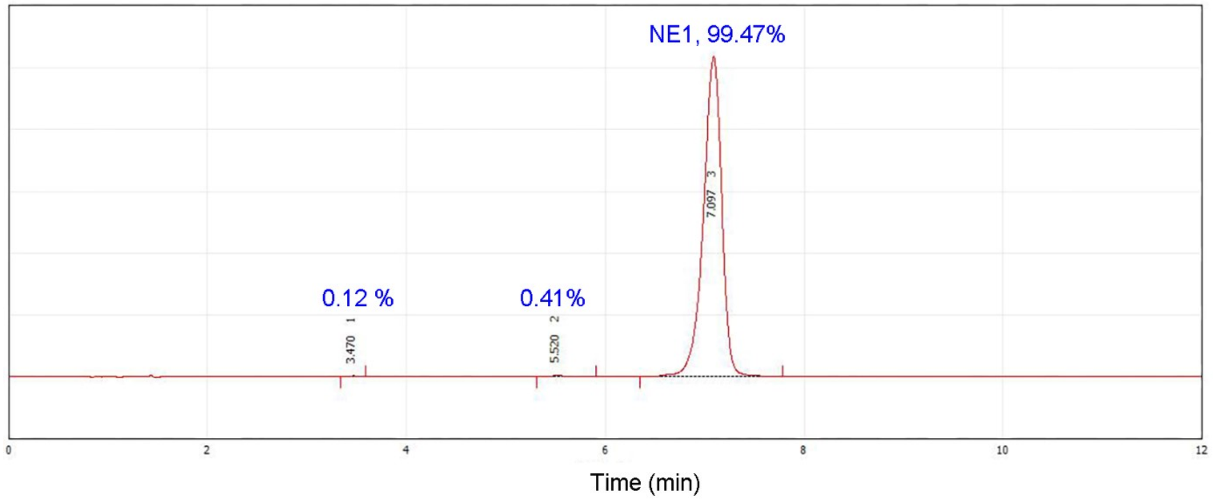


Figure S8. HPLC chromatogram and peak area percentage analysis of NE1 purified by recrystallization.

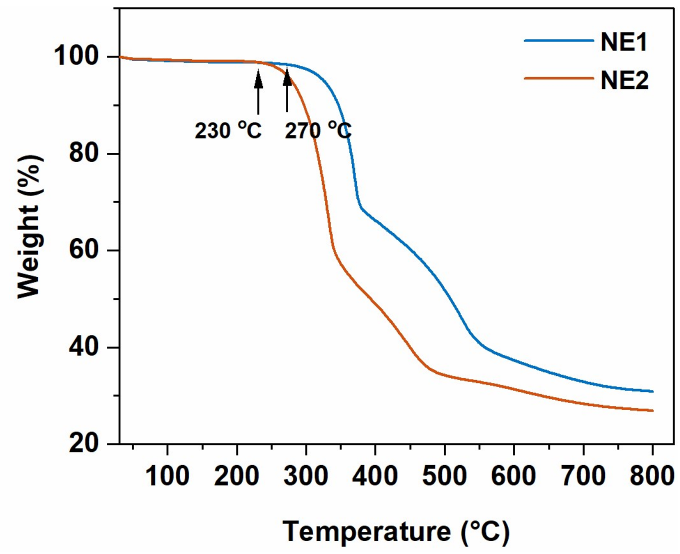


Figure S9. Thermogravimetric curves of NE1 and NE2.

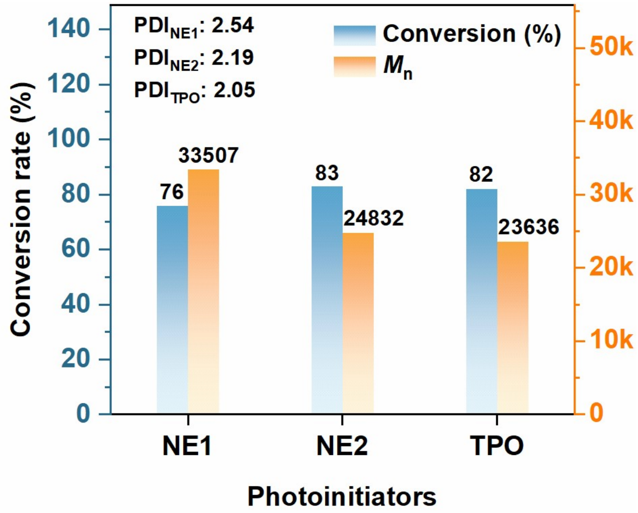


Figure S10. Monomer conversion rate, number average molecular weight (M_n), and polydispersity index (PDI) of polymers obtained from the photopolymerization of *tert*-butyl acrylates with NE1, NE2, and TPO.

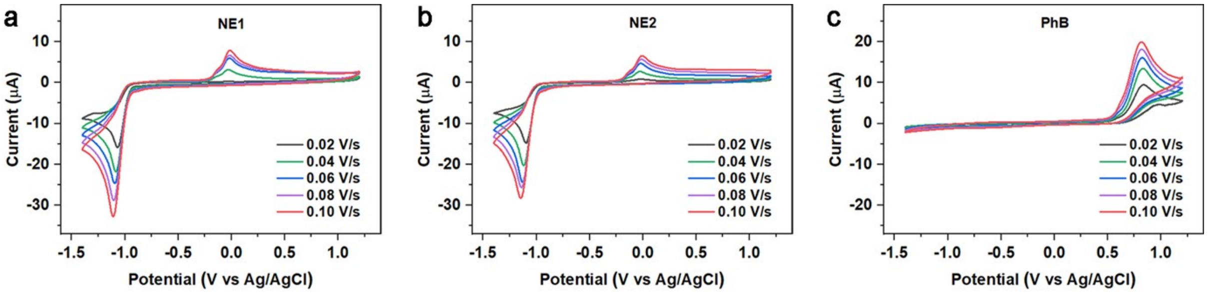


Figure S11. Cyclic voltammetry curves of NE1, NE2, and PhB in dichloromethane.

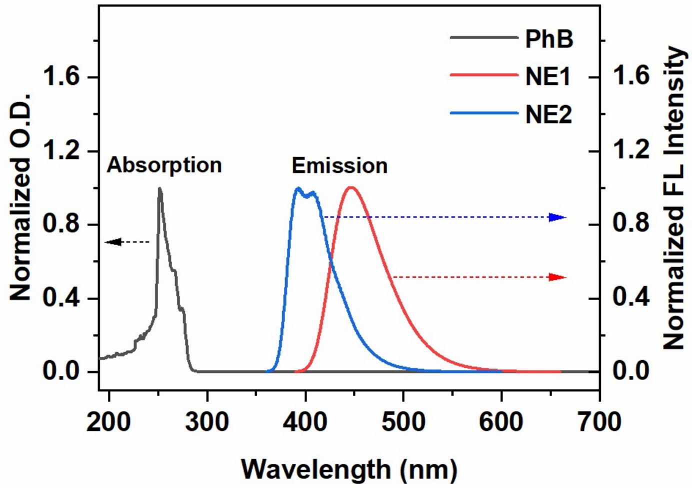


Figure S12. Emission spectra of NEs and UV-vis absorption spectra of PhB in ethyl acetate.

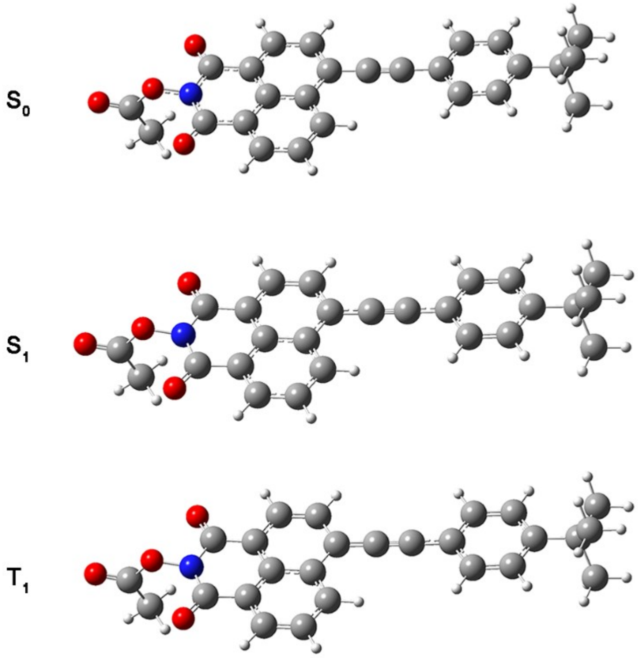


Figure S13. Optimized geometries of NE1 in the ground state (S_0), singlet state (S_1), and triplet state (T_1). (Color code: gray ball, C; red ball, O; blue ball, N; white ball, H).

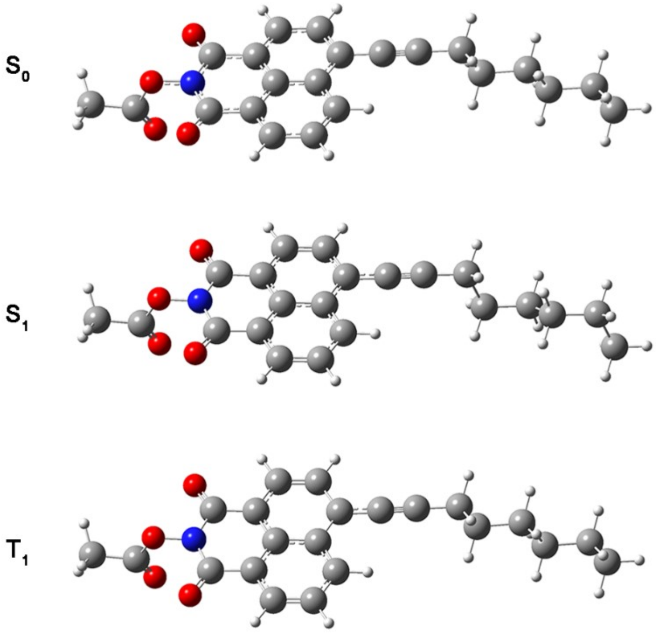


Figure S14. Optimized geometries of NE2 in the ground state (S$_0$), singlet state (S$_1$), and triplet state (T$_1$). (Color code: gray ball, C; red ball, O; blue ball, N; white ball, H).

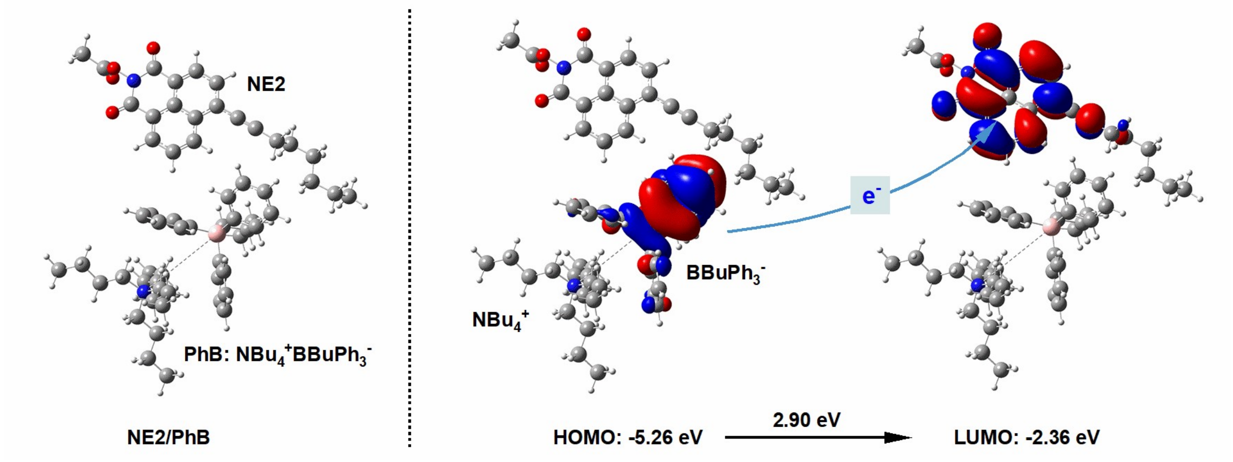


Figure S15. Optimized structure and front orbitals of NE2/PhB complex. (Color code: gray ball, C; red ball, O; pink ball, B; blue ball, N; white ball, H).

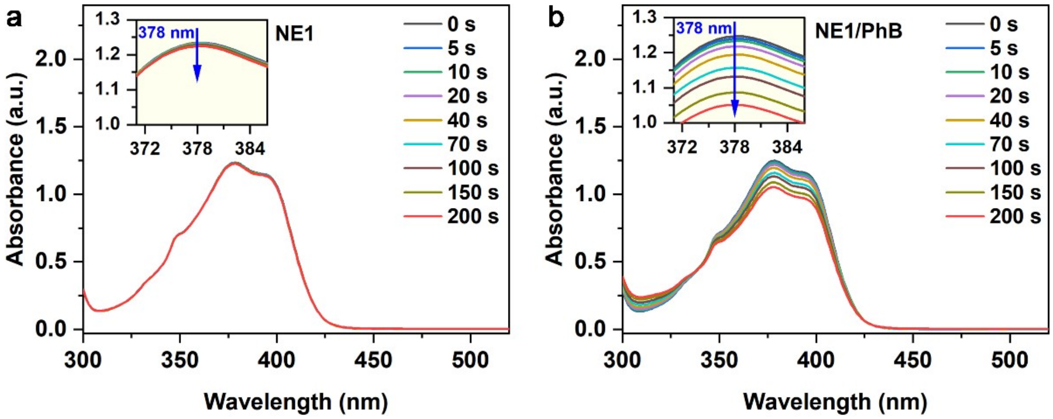


Figure S16. UV-vis absorption spectra of (a) NE1 and (b) NE1/PhB in ethyl acetate under 405 nm LED irradiation. [NE1] = 5 × 10^{-5} M, [PhB] = 5 × 10^{-5} M.

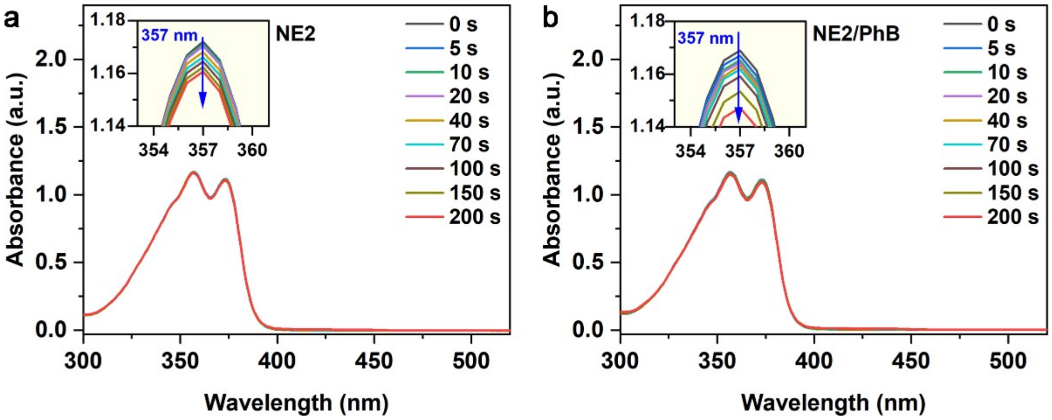


Figure S17. UV-vis absorption spectra of (a) NE2 and (b) NE2/PhB in ethyl acetate under 405 nm LED irradiation. [NE2] = 5 × 10^{-5} M, [PhB] = 5 × 10^{-5} M.

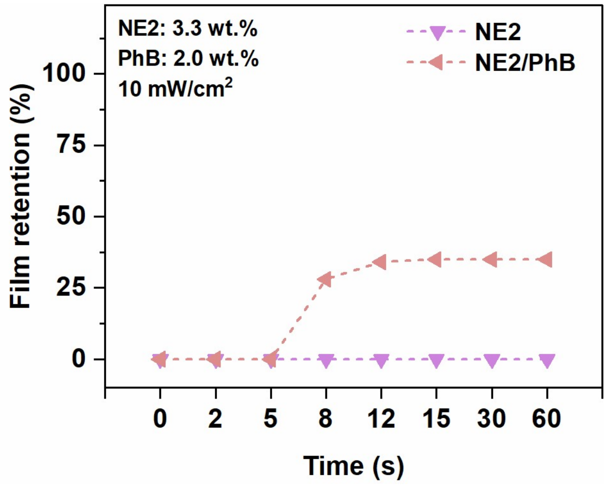


Figure S18. Correlation between film retention rate and irradiation time for NE2- and NE2/PhB-involved photoresists under 405 nm exposure with a film thickness of about 700 nm.

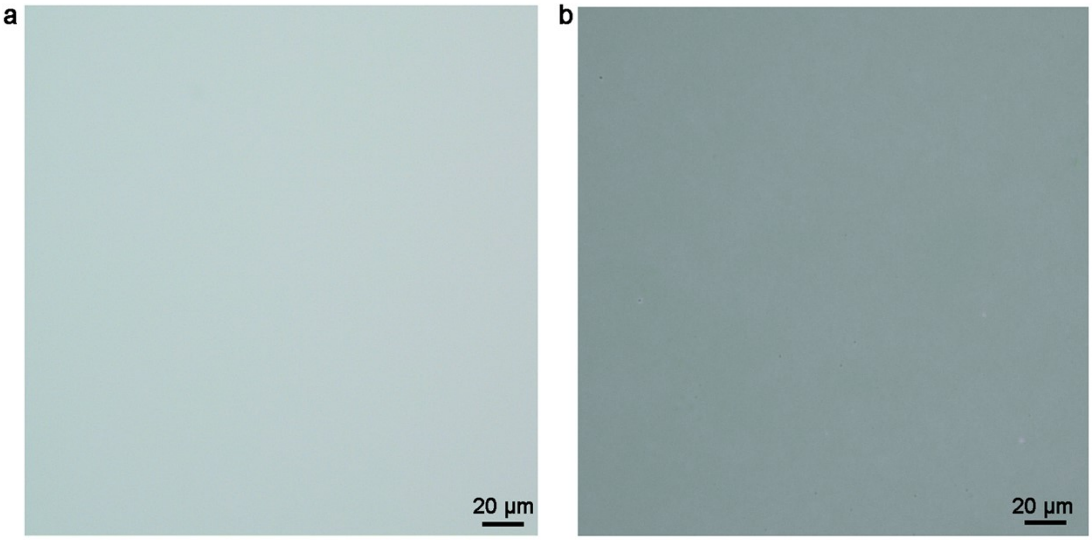


Figure S19. (a) Optical microscope image of NE1/borate-photoresist coating, (b) optical microscope image of NE1/borate-photoresist film after irradiation with a 405 nm LED and immersion in alkaline water for 60 s.

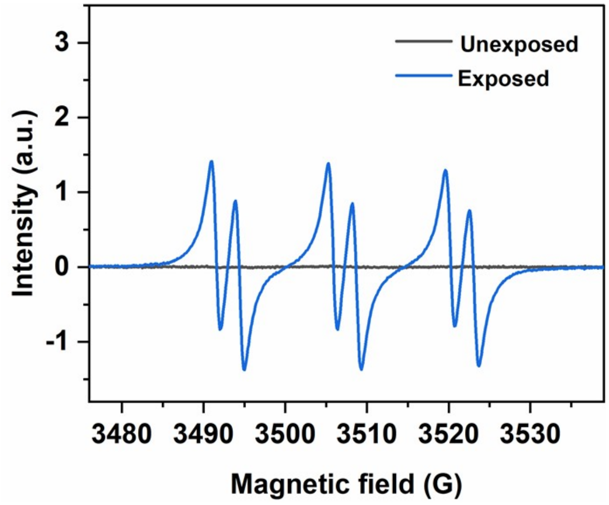


Figure S20. ESR spectra of NE1 in the presence of α-phenyl-N-tert-butyl nitrone (PBN) and in toluene.

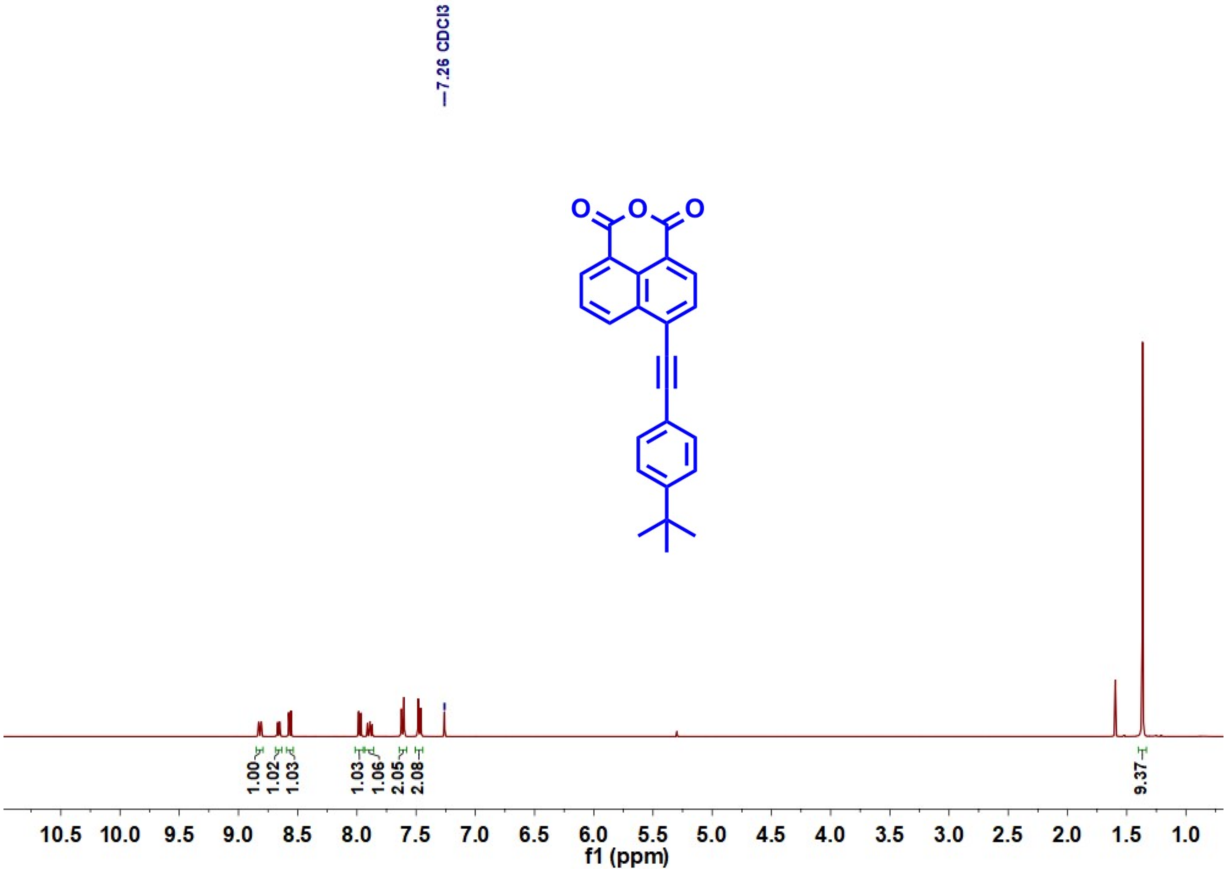


Figure S21. ^{1}H NMR spectrum of NO.

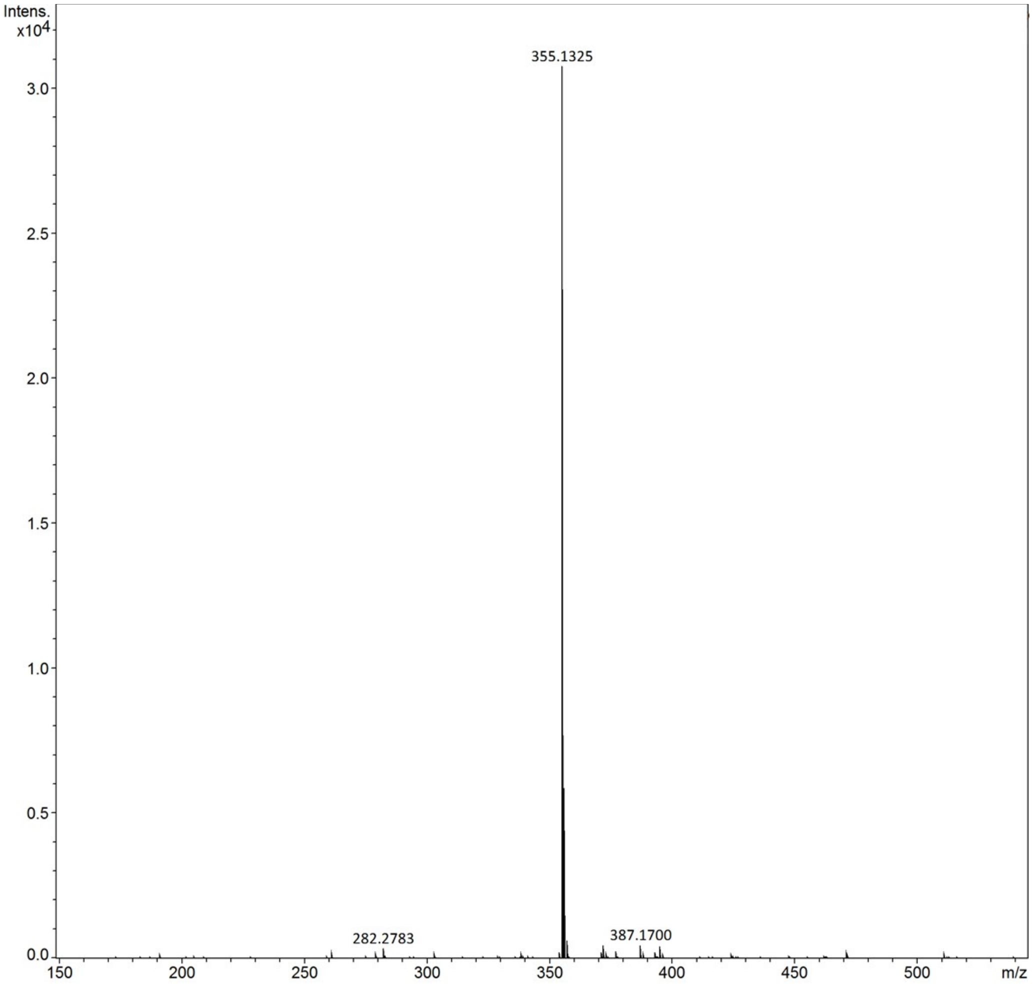


Figure S22. High-resolution mass spectrum of NO. Theor: 354.1256, found (M + H$^+$. detected): 355.1325.

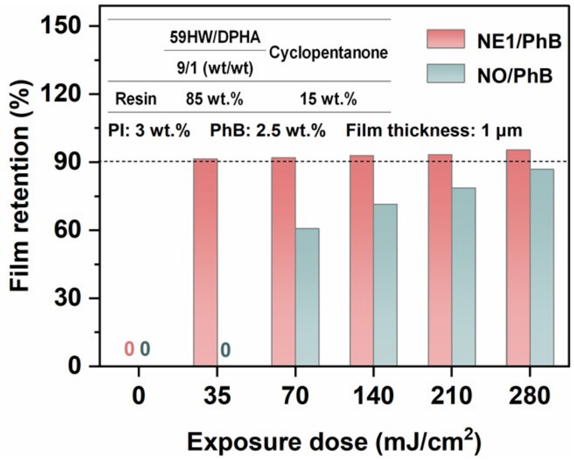


Figure S23. Film retention rates of NO/PhB and NE1/PhB-based photoresists after 405 nm LED irradiation with a light intensity of 35 mW/cm^2, followed by 90 s immersion in alkaline solution. 59HW resin stands for CCR-4959HW.

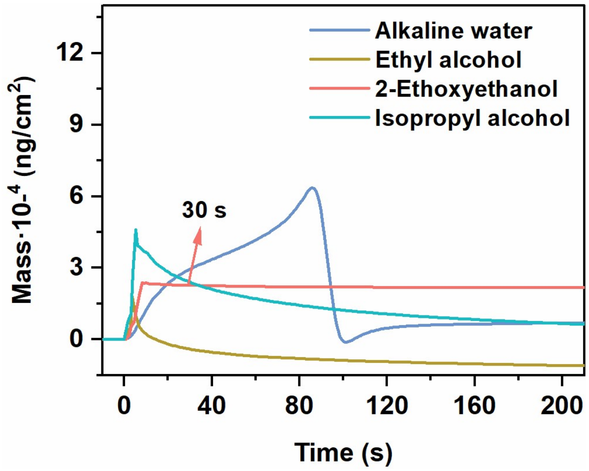


Figure S24. QCM curves of NE1/PhB-involved photoresist films during the development process in alkaline water, ethyl alcohol, 2-ethoxyethanol, and isopropyl alcohol.

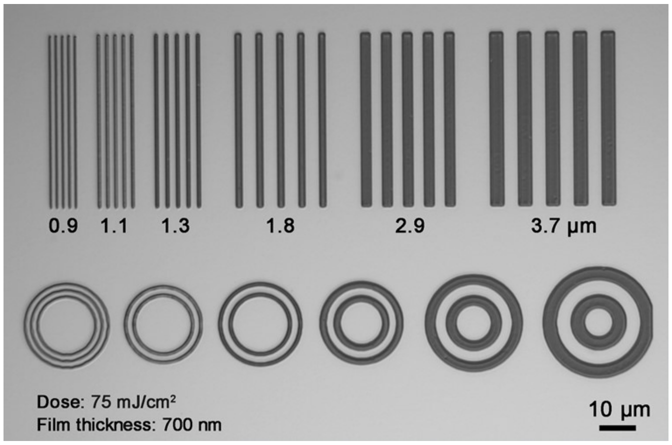


Figure S25. Optical microscope image of patterns obtained by irradiation in air using NE1/PhB-involved photoresist. [NE1] = 3.3 wt.%, [PhB] = 2.0 wt.%.

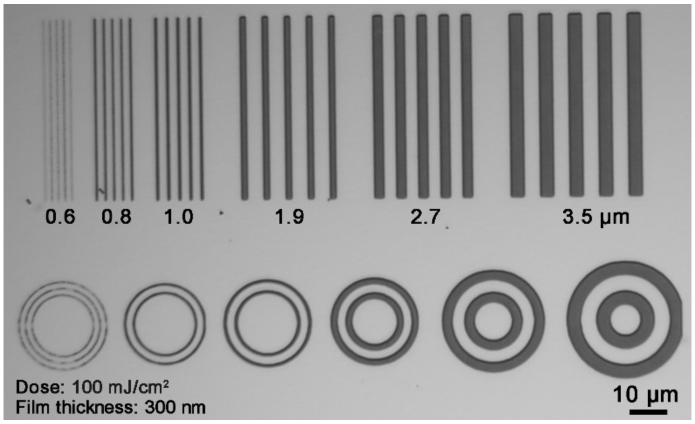


Figure S26. Optical microscope image of patterns obtained by irradiation in air using NE1/PhB-involved photoresist. [NE1] = 5.0 wt.%, [PhB] = 3.3 wt.%.

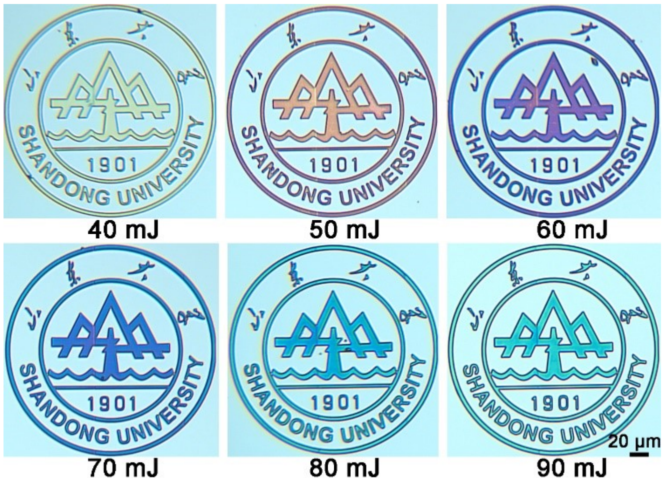


Figure S27. Optical microscope images of patterns developed from NE1/PhB-based photoresists at exposure doses of 40~90 mJ/cm^2. [NE1] = 5.0 wt.%, [PhB] = 3.3 wt.%.

4. Supporting Tables

Table S1. Photophysical parameters of NEs.

Parameters	NAc	NE1	NE2
λ_{max} (nm)	341	378	357
ε_{max} (M^{-1} cm^{-1})	20,817	24,687	23,473
$\varepsilon_{365\ nm}$ (M^{-1} cm^{-1})	4,279	19,750	19,636
$\varepsilon_{395\ nm}$ (M^{-1} cm^{-1})	–	22,854	498
$\varepsilon_{405\ nm}$ (M^{-1} cm^{-1})	–	16,763	86
$\varepsilon_{455\ nm}$ (M^{-1} cm^{-1})	–	67	–
$\lambda_{cut\text{-}off}$ (nm)	386	495	425
τ_0 (ns)	0.4	2.5	2.4

Table S2. Electrochemical parameters and free energy change.

NEs	$E_{1/2red}$ (V)	BDE (eV) Ground	BDE (eV) Triplet	E_{S1} (eV)	E_{T1} (eV)	ΔG_{S1} (eV)	ΔG_{T1} (eV)	ΔH_{S1} (eV)	ΔH_{T1} (eV)
NE1	-1.01	2.29	0.46	2.74	1.79	-1.01	-0.06	-0.45	-1.33
NE2	-1.04	2.51	0.53	3.08	1.93	-1.32	-0.17	-0.57	-1.40

Evaluated from $\Delta G = E_{ox}$ (PhB) - E_{red} (NEs) - $E_{S1/T1} + C$, $C \approx 0$. $E_{1/2ox}$ (PhB) =0.72 V. Calculated ΔG value considering the electrochemical half-wave potential ($E_{1/2ox}$ and $E_{1/2red}$). ΔH_{S1}=BDE(N–O)$_{ground}$ - E_{S1}. ΔH_{T1} =BDE(N–O)$_{triplet}$ - E_{T1}.

Table S3. Composition of the photoresist with a solid content of 15 wt.%.

	CCR-4959HW/DPHA 9/1 (wt/wt)	Solvent
Resin system	15 wt.%	85 wt.%

The solvent in the photoresist formulation is PGMEA.

Table S4. Composition of the photoresist with a solid content of 35 wt.%.

	CCR-4959HW/DPHA	Solvent
	9/1 (wt/wt)	
Resin system	35 wt.%	65 wt.%

The solvent in the photoresist formulation is cyclopentanone.

Table S5. Comparative analysis of photoresist film retention rate under LED@405 nm irradiation across diverse photoinitiators.

PI	Film retention rate (%)
NE1/PhB	96.9
NE1/TCTA	92.3
NE1/TBATPB	88.9
TPO	6.3
TPO/PhB	6.1

A photoresist film with a thickness of approximately 5.3 μm was cured using a 405 nm LED (exposure dose of 50 mJ/cm^2) and then immersed in an alkaline solution for 120 s. Keep the molar addition amounts of TPO and NE1 the same.

References

[1] K. Teng, D. Zhang, B. Liu, Z. Liu, L. Niu and Q. Yang, *Angew. Chem. Int. Ed.*, 2024, **63**, e202318783.