

Supporting Information

CuBr-mediated surface-initiated controlled radical polymerization in air

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1. Materials:

Monomers: N-isopropyl acrylamide (NIPAAm), (methacryloyloxy)ethyl trimethylammonium chloride (METAC), 3-[Dimethyl-[2-(2-methylprop-2-enoyloxy)ethyl]azaniumyl]propane-1-sulfonate (SBMA), 3-sulfopropyl methacrylate potassium salt (SPMA), 2-hydroxyethyl methacrylate (HEMA), poly(ethylene glycol) methyl ether acrylate (OEGA), poly(ethylene glycol) methyl ether methacrylate (OEGMA), N-(1,1-Dimethyl-3-oxobutyl)acrylamide (NDOA), were used as received. Methyl methacrylate (MMA), methyl acrylate (MA), and tert-butyl methacrylate (tBuMA) were purified by passing through a basic alumina column.

Silicon wafers with an oxide layer (~285 nm) (Si/SiO₂) were purchased from Wacker AG (Burghausen, Germany). Methanol, trichloromethane, potassium persulfate (KPS), 2-bromo-2-methyl-6-trimethoxysilylhexanoate, the ligand 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA) were used as received.

2. Surface characterization

The thickness and morphology of polymer brushes on the silicon substrate were characterized by atomic force microscopy (AFM) or ellipsometry (ESM-300, J. A. Woollam Co., Inc. Equipped with angles of incidence of 60° and 70°). Measurements

were performed at least three times at different locations of three samples.

The chemical compositions of the samples were determined from X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi) measurements.

The infrared spectra were obtained by infrared spectrophotometer (Niconet iS 10, Thermo Scientific).

The surface wettability was measured on the same substrate at five different positions with a DSA 100 (Kruss company, Germany) using a 5 μ L distilled water droplet at ambient temperature.

3. Methods

3.1 Self-assembled monolayer (SAM) of initiator on the substrates

Silicon wafers were washed alternately with distilled water and ethanol for 5 min, and then ionized by oxygen plasma (Zepto One, Diener company) for 15 min and dried with N₂ stream. The cleaned substrates were functionalized with 3-(Trimethoxysilyl)propyl-2-bromo-2-methylpropanoate by vapor deposition for 6 h inside an oven at 90°C.^[1] The functionalized silicon wafers were ultrasonically cleaned with ethanol and distilled water and then dried with a dry N₂ flow.

3.2 Synthesis of PMMA

KPS solution was prepared by dissolving 0.0595 g KPS in 10 mL distilled water. The 10 mL purified MMA and 30 mL distilled water were added to a 100 mL RBF along with a stir bar. The mixture was purged with N₂ for 30 minutes in the 80 °C water bath and then KPS solution was added dropwise. After 6 h, PMMA was obtained.

3.3 Preparation of CuBr films

Preparation of CuBr/PMMA film: PMMA was dissolved in trichloromethane, and then grinding CuBr were added to the solution. After mixing well, about 0.2 mL of CuBr/PMMA solution was dropped into the cover glass and placed on the spinning

coating machine. A uniform CuBr/PMMA film was obtained after spin coating at a certain speed.

Preparation of CuBr/PDMS film: 0.15 g CuBr was mixed with 1.5 g polydimethylsiloxane (PDMS), followed with 0.15 g curing agent. Then about 0.2 mL of the mixture was dropped into the cover glass placed on the spinning coating machine. After that, the film was heated at 80°C for 90 min.

Preparation of CuBr/PDMS film: The CuBr₂ solutions with a concentration of 0.01 M were prepared. The Cu films deposited by sputtering were immersed in the solution for 300 s, resulting in porous CuBr films. The prepared films were cleaned by dipping them in a Petri dish containing pure methanol (10 mL) for 60 s and then dried in a vacuum oven at 70 °C. [2]

3.3 Polymerization solution and setup for CuBr-mediated SI-CRP

The normal polymerization solution was prepared by adding monomer, ligand, and solvent. For HEMA, OEGA, OEGMA, METAC: 0.5 mL monomer, 1.5 mL solvent (water: methanol=2: 1), 10 µL PMDETA. For SBMA, SPMA, NDOA: 0.5 g monomer, 1.5 mL solvent (water: methanol=2: 1), 10 µL PMDETA. For NIPAM: 0.25 g monomer, 1.5 mL solvent (water: methanol=2: 1), 10 µL PMDETA. For MMA, MA, tBuMA: 80 µL monomer, 1.5 mL solvent (water: methanol=2: 1), 10 µL PMDETA and the mixture was stirred vigorously for 5 min at room temperature. After standing for 30 min, the supernatant was taken to participate in the reaction. [3]

CuBr film was sandwiched with the silicon wafer piece modified with the initiator at a certain distance (normally 0.18 mm if not specially mentioned). Then the polymerization solution is injected into the sandwich assembly followed by polymerization for a certain time (30 min if not specially mentioned) under ambient conditions. After that, the substrate was extensively washed with distilled water and ethanol and dried under N₂ stream.

3.5 In-situ chain growth of polymer brushes

The polymerization solution was prepared by 0.5 mL OEGMA, 10 μ L PMDETA, and solvent. The first segment of POEGMA brushes was prepared catalyzed by $\text{CuBr}_{0.1}$ at a distance of 0.49 mm for 15 min. The substrate was washed and then subjected to a second reaction of OEGMA solution for another 45 min.

To explore the reason for the low growth rate of the PSPMA brushes catalyzed by $\text{CuBr}_{0.5}$, the in-situ chain growth of PSPMA brushes proceeded. The first segment of PSPMA brushes was prepared by SI-CRP catalyzed by $\text{CuBr}_{0.5}$ at a distance of 0.13 mm for 30/60 min. The substrate was washed and then subjected to a second reaction of SPMA solution for another 30/60 min.

3.6 Fabrication of multiblock copolymer brushes

The polymerization solution was prepared by 0.5 mL of OEGA, 10 μ L of PMDETA, and solvent. The first block of POEGA brushes was prepared by SI-CRP catalyzed by $\text{CuBr}_{0.1}$ at a distance of 0.49 mm for 15 min. The substrate was washed and then subjected to a second reaction of OEGMA solution for another 45 min and cleaned again.

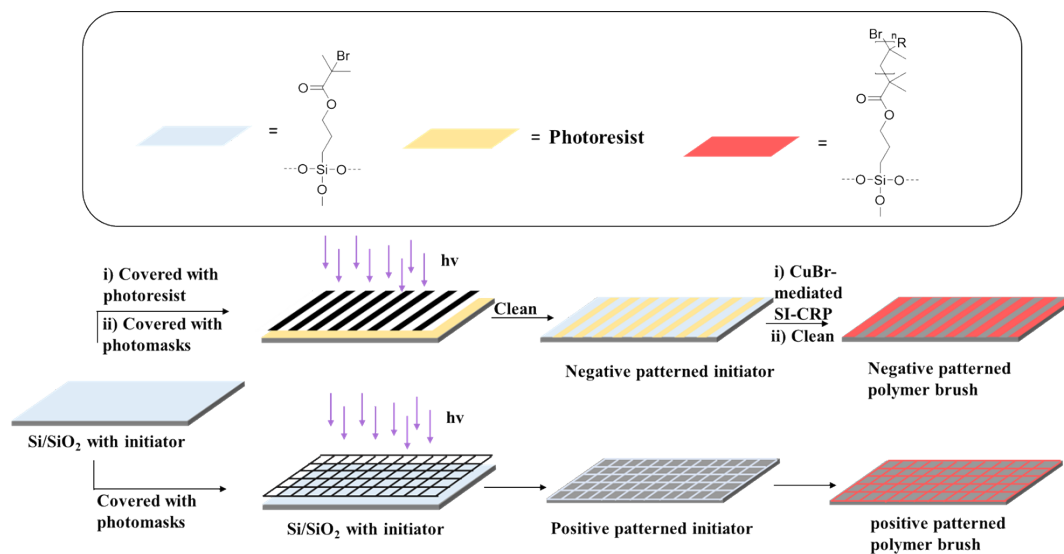
3.7 Fabrication of patterned polymer brushes

A photomask with complex structures and a gold grid with microscopic regular square holes was used for the patterned substrate.

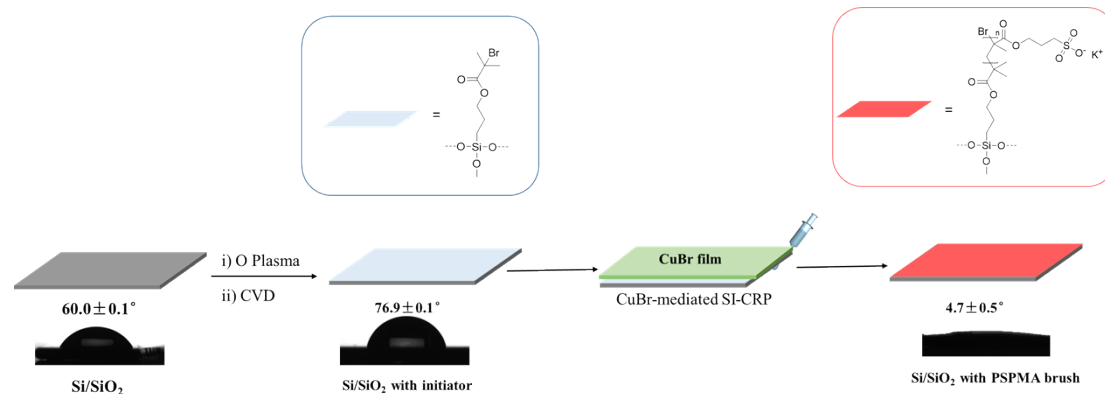
For the positive pattern, the initiator-functionalized substrate was spin-coated with the positive photoresist (BP-212). After UV irradiation through a photomask and cleaning, a patterned photoresist on the substrate was prepared. Polymer brush grows in exposed areas of substrates by CUBR-MEDIATED SI-CRP as mentioned above. Finally, the remaining photoresist was removed and negative patterns were obtained.

For the negative pattern, the initiator-modified substrate was patterned as above. After oxygen plasma treatment, the initiator in exposed areas of photoresist was removed.^[2] Then the remaining photoresist was removed and the positive patterned polymer

brush was obtained by CuBr-mediated SI-CRP.



4. Supporting graphs and tables



Scheme S1. The process of the immobilizing initiator onto the Si/SiO₂ wafer and CuBr-mediated SI-CRP and the change of water contact angle of Si/SiO₂ wafers after each operation.

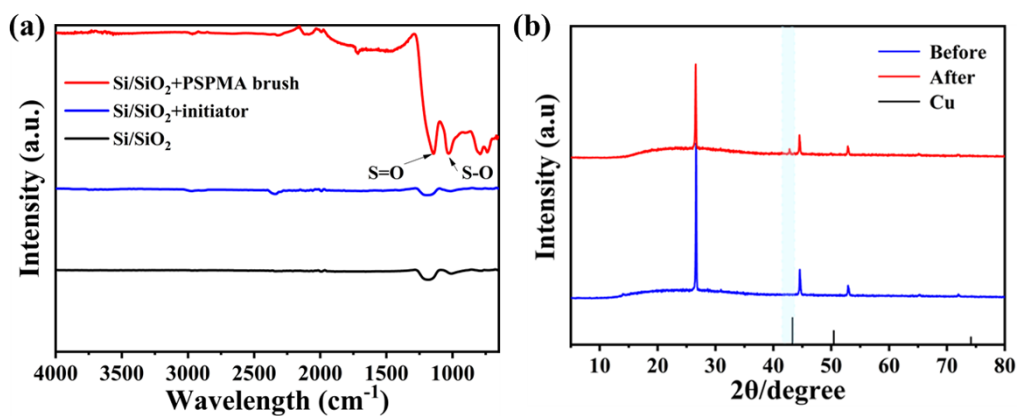


Figure S1. (a) Comparison of FTIR spectra of silicon wafers before and after the load of the initiator and the synthesis of polymer brushes. (b) XRD spectra of CuBr_{0.5} before and after use as catalyst.

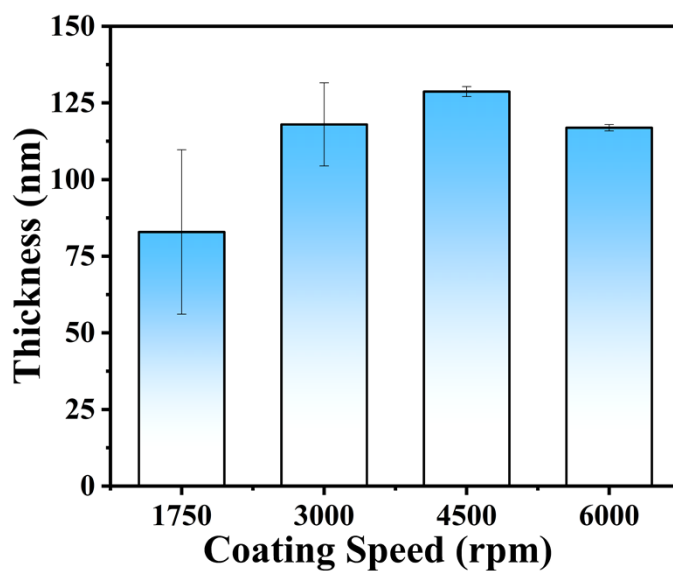


Figure S2. Comparison of PSPMA brush grafting via CuBr-mediated SI-CRP where CuBr films prepared by different coating speeds.

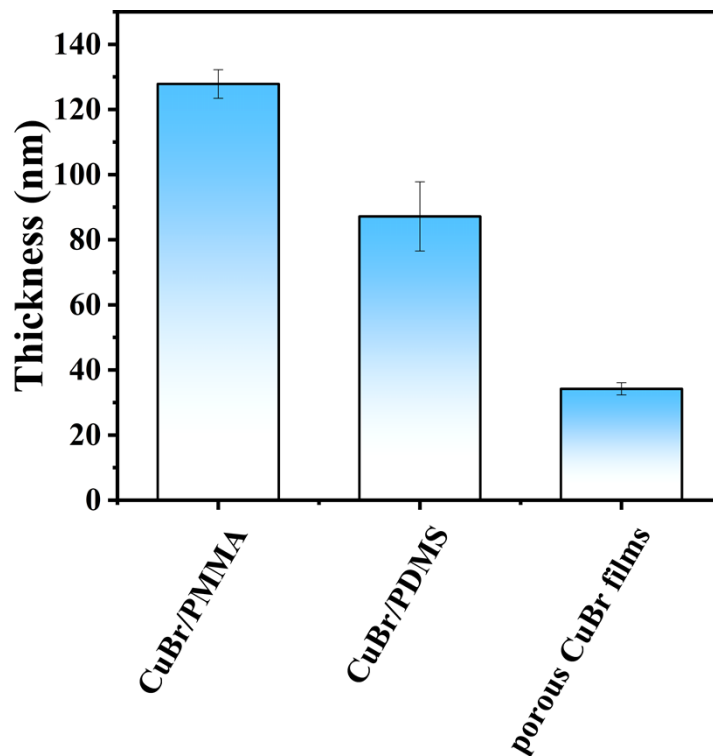


Figure S3. Comparison of PSPMA brushes via different CuBr film (CuBr/PMMA, CuBr/PDMS and porous CuBr film) (PMDETA:20 μ L, polymerization: 30 min)

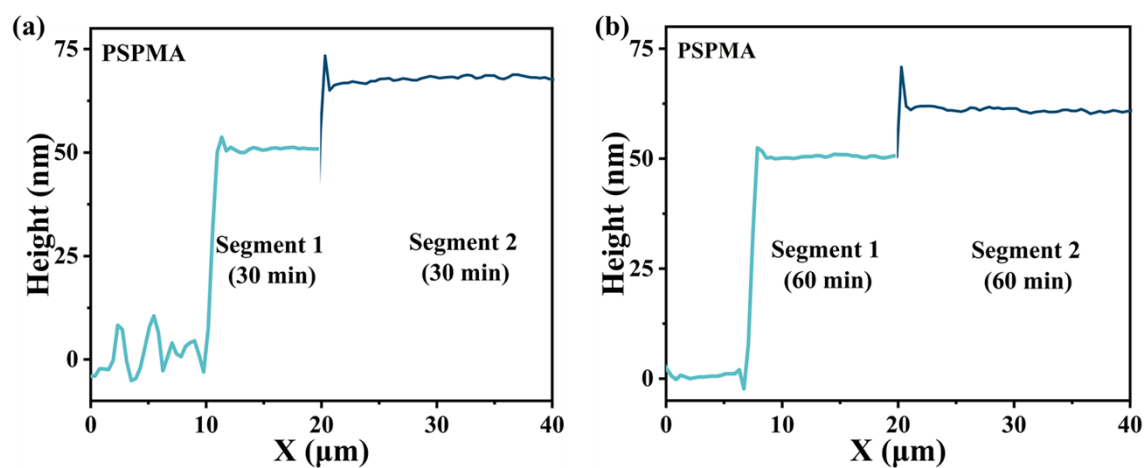


Figure S4. The end-group fidelity of the PSPMA brushes catalyzed by $\text{CuBr}_{0.5}$: The thickness of two segments of PSPMA brushes (each segment was obtained after 30-min (a) or 60-min (b) reactions, PMDETA:10 μ L).

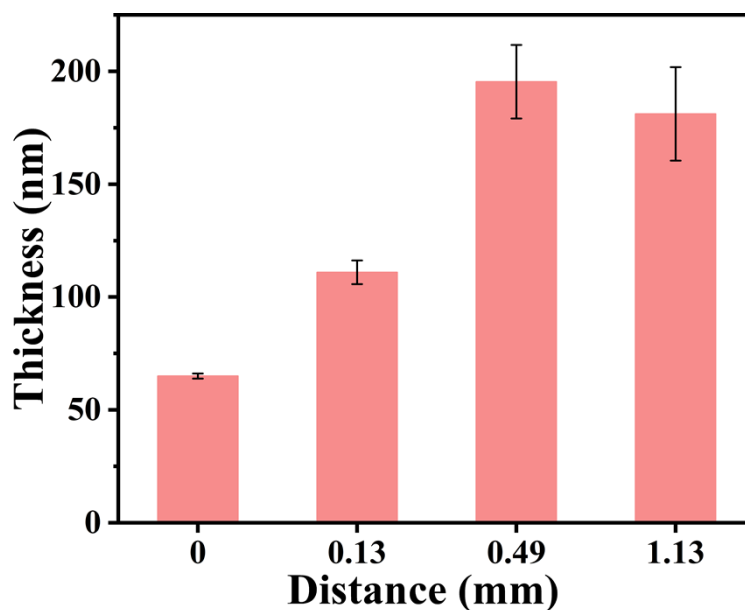


Figure S5. Influence of the distance on the CuBr-mediated SI-CRP of SPMA via CuBr_{0.1} (PMDETA:20 μ L, polymerization: 30 min)

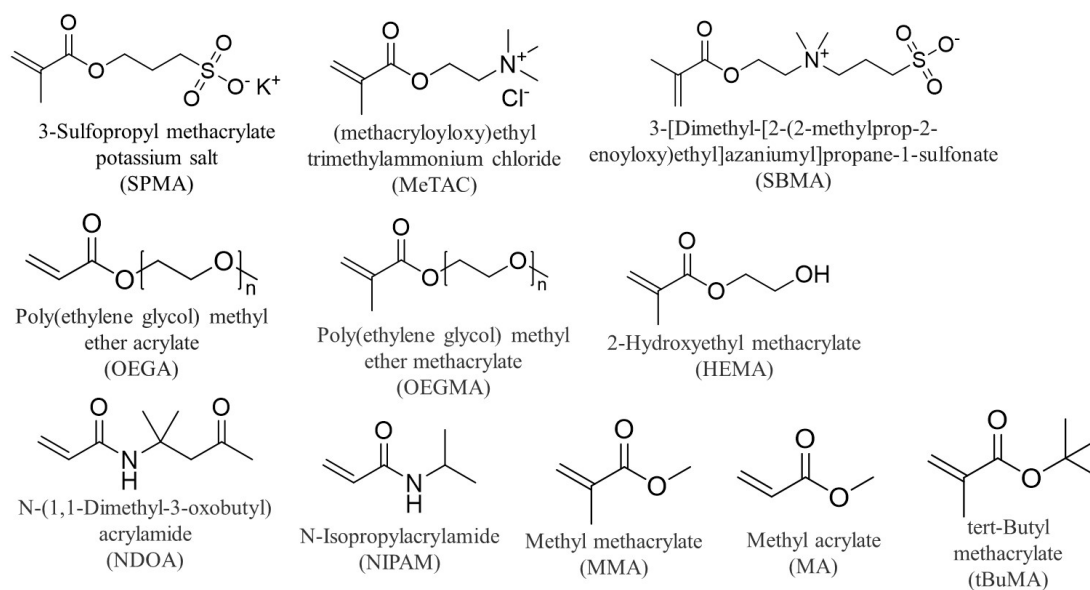


Figure S6. Chemical structures of monomers used for CuBr-mediated SI-CRP.

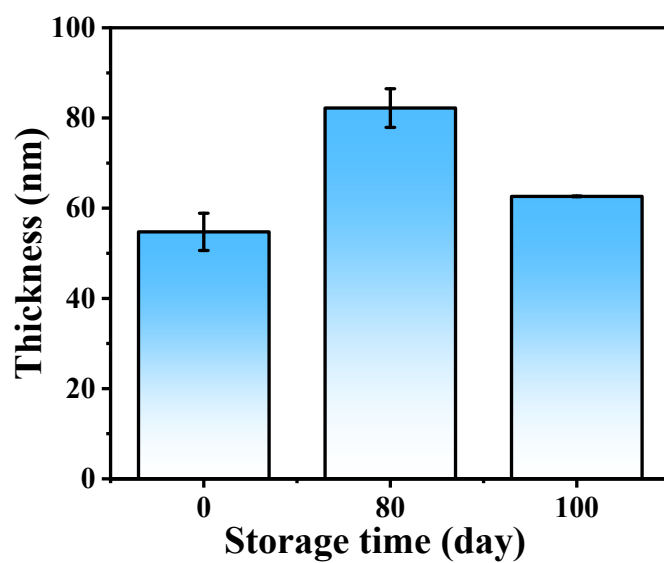


Figure S7. Comparison of PSPMA brush grafting via SI-ATRP catalyzed by fresh CuBr film and that stored 80 days and 100 days.



Figure S8. Optical micrographs of large-sized pattern PSPMA brushes.

Table S1. Calculation of CuBr per unit area and the solution utilization.

CuBr film	Membrane weight (mg)	CuBr weight (mg)	CuBr/S ^a ($\mu\text{mol}/\text{cm}^2$)	Solution utilization ^b (%)
CuBr _{0.025}	3.05 \pm 0.11	0.28 \pm 0.01	0.31 \pm 0.01	20.77 \pm 1.44
CuBr _{0.1}	3.10 \pm 0.00	0.89 \pm 0.00	0.99 \pm 0.00	16.77 \pm 4.54
CuBr _{0.5}	6.64 \pm 0.27	4.43 \pm 0.18	4.94 \pm 0.20	16.21 \pm 2.02

a. S means the value of the area covered by the membrane. S=6.25 cm².

b. Solution utilization (%) = Membrane weight/the weight of dropwise solution.

Table S2. Grafting density of polymer brushes via SI-CRP catalyzed by CuBr_{0.025}/CuBr_{0.1}/CuBr_{0.5}.

CuBr film	h_{dry} (nm)	h_{swollen} (nm)	$h_{\text{swollen}}/h_{\text{dry}}$	Polymerization degree, N ^a	Grafting density ^b (chains/nm ²)
CuBr _{0.025}	125.35 \pm 45.0	914.00 \pm 284.3	7.29	26507.05	0.02
CuBr _{0.1}	72.17 \pm 16.2	150.00 \pm 17.0	2.08	2322.59	0.11
CuBr _{0.5}	39.23 \pm 4.6	90.83 \pm 8.1	2.32	1484.38	0.09

- a. Polymerization degree $N = [1.074(h_{\text{swollen}})^{3/2}]/[(h_{\text{dry}}(\text{\AA}^2))^{1/2}]$ (the constant related to excluded volume parameter, 1.074 was used independently of the type of monomers)
- b. Grafting density $\sigma = [\rho_{\text{dry}}N_{\text{A}}]/[M_0N]$ (N: degree of polymerization, σ : polymer density, N_{A} : Avogadro's number, M_0 : monomer molecular weight) ^[5]

References:

- [1] D. Wu, X. Yin, Y. Zhao, Y. Wang, D. Li, F. Yang, L. Wang, Y. Chen, J. Wang, Yang, X. Liu, F. Liu, T. Zhang, *ACS Macro Lett.* **2023**, 12, 71–76.
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