Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Self-Contained Photoacid Generator for Super Acid Based on Photochromic Terarylene

Ruiji Li,[a] Takuya Nakashima,*[a] and Tsuyoshi Kawai*[a,b]

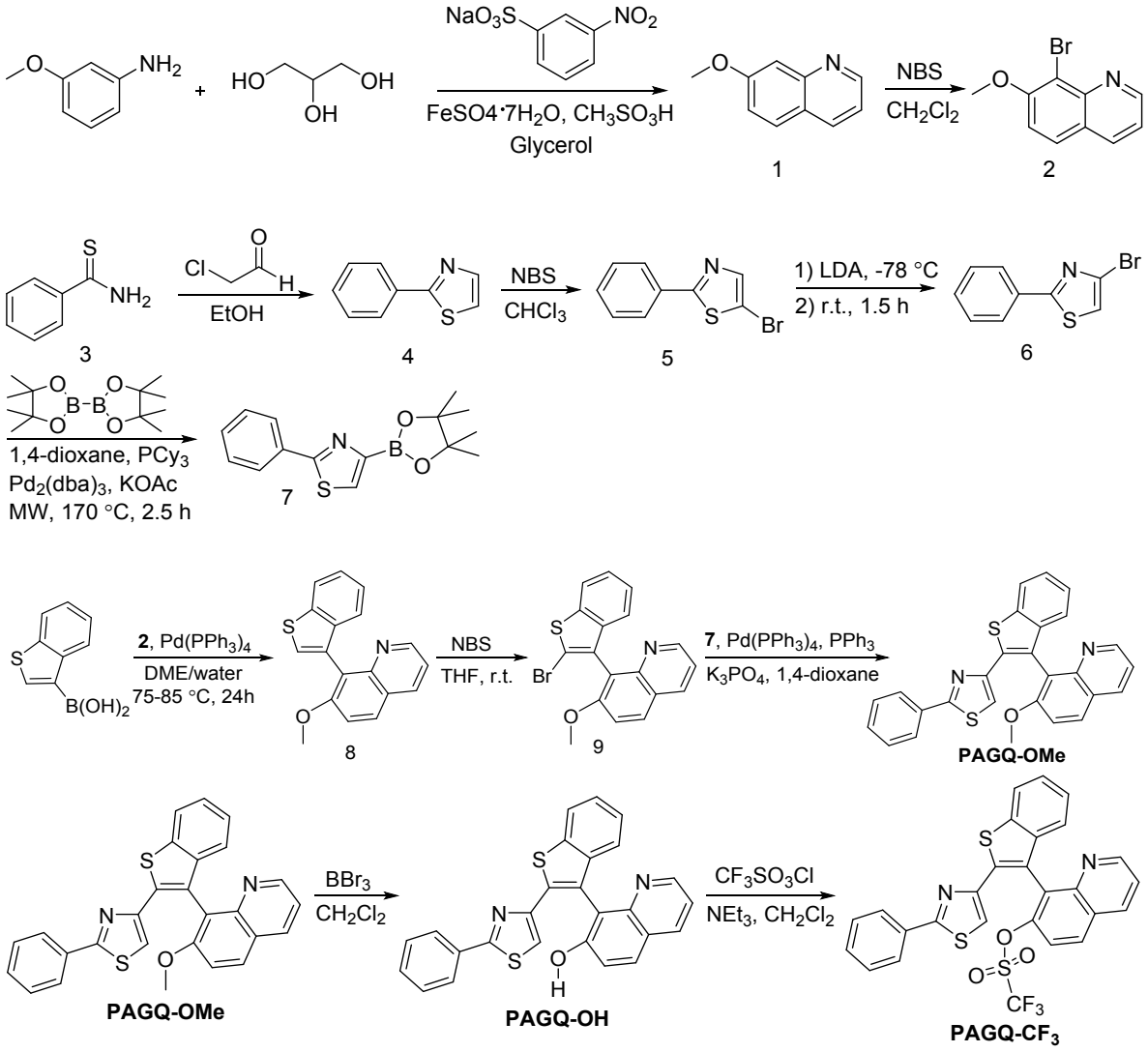
[a.] *Graduate School of Materials Science, Nara Institute of Science and Technology, Ikoma, Nara 630-0192, Japan. E-mail: ntaku@ms.naist.jp, tkawai@ms.naist.jp.*
[b.] *NAIST-CEMES International Collaborative Laboratory, CEMES-CNRS (UPR 8011) Toulouse 31055, France.*

1.1 Experiments

1.1.1 General

Compounds were synthesized according to the reaction procedures as showed in Scheme S1. Their chemical structures were confirmed by ^{1}H NMR (400 MHz) and ^{13}C NMR (75 MHz) spectroscopy on JEOL JNM-ECP400 and JNMAL300 spectrometers, respectively. High-resolution mass spectrometry (HRMS) analyses were performed on a JEOL JMS-700 mass spectrometer. Separative HPLC was performed on a JASCO LC-2000 Plus Series. Absorption spectra in solution were studied with a JASCO V-670 spectrophotometer. Quantum yields were measured with QYM-01 photoreaction quantum yield evaluation system (λ = 313 nm).[1]

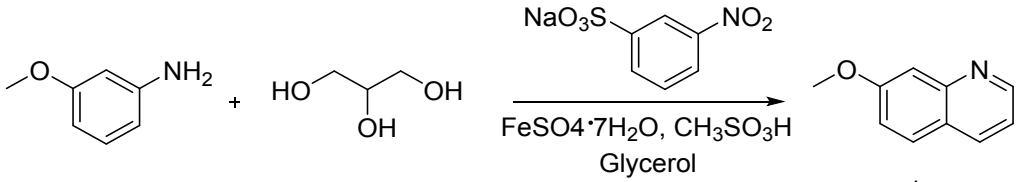
1.1.2 Synthesis



Scheme S1. Synthetic scheme of **PAGQ-CF$_3$**

Compounds **4**, **5**, **6** and **7** were synthesized as described in the literature.[2,3,4]

Synthesis of 7-methoxyquinoline **(1)**



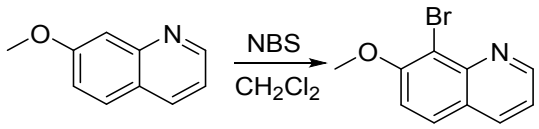
1

100 mL 3-neck flask was charged with sodium m-nitrobenzenesulfonate (3.9g, 17.3 mmol) and methanesulfonic acid (10 mL) stirred at room temperature. Then $FeSO_4 \cdot H_2O$ (0.2 g, 0.8 mmol) and 3-methoxyaniline (3.09 mL, 27.5 mmol) were added to the mixture. The mixture was heated to 118-125 °C. After that glycerol (6.3 g, 68.8 mmol) was added to the mixture. Then the mixture was heated up to 135 °C and keep at this temperature for 16 h (monitored by TLC analysis). After the reaction the mixture cool to room temperature and 10 M NaOH solution was added to mixture to dilute the viscous mixture. Then the mixture was extracted with ethyl acetate. The organic layer was dried with anhydrous magnesium sulfate and the crude product was purified by silica gel chromatography (hexane/EtOAc = 7:3) to get compound **1** (4.2 g, 48 %) as yellow oil.

^{1}H-NMR (300 MHz, TMS, $CDCl_3$) δ: 3.96 (s, 3H), 7.19-7.29 (m, 2H), 7.43(sd, 1H), 7.68-7.71 (d, 1H, J = 9 Hz), 8.06-8.09 (d, 1H, J = 9 Hz), 8.83-8.85 (d, 1H, J = 9 Hz).

ESI-HRMS: calcd for $C_{10}H_{10}NO^+$ $[M+H]^+$ 160.07624; found 160.07621.

Synthesis of 8-bromo-7-methoxyquinoline **(2)**



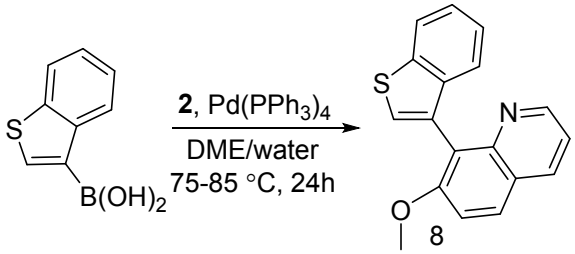
1 2

100mL 3-neck flask was charged with compound **1** (4.2 g, 26.4 mmol), and NBS (5.7 g, 31.68 mmol). Dichloromethane (60 mL) was added to the mixture and the mixture was stirred at 0 °C for a while under argon gas atmosphere. Then the mixture was stirred at room temperature for overnight (monitored by TLC analysis). After the reaction, $Na_2S_2O_3$ aq. was added to the mixture and extracted with dichloromethane. Then the organic layer was dried with anhydrous magnesium sulfate and the crude product was purified by silica gel chromatography (hexane/EtOAc = 3:1) to get compound **2** (5.9 g, 93.1 %) as colorless solid.

^{1}H-NMR (300 MHz, TMS, $CDCl_3$) δ: 4.09 (s, 3H), 7.33-7.39 (m, 2H), 7.81-7.84 (d, 1H, J = 9 Hz), 8.12-8.15 (d, 1H, J = 9 Hz), 9.03-9.04 (d, 1H, J = 3 Hz).

EI-HRMS: calcd for $C_{10}H_8BrNO^+$ $[M]^+$ 236.97893; found 236.97833.

Synthesis of 8-(benzo[*b*]thiophen-3-yl)-7-methoxyquinoline **(8)**

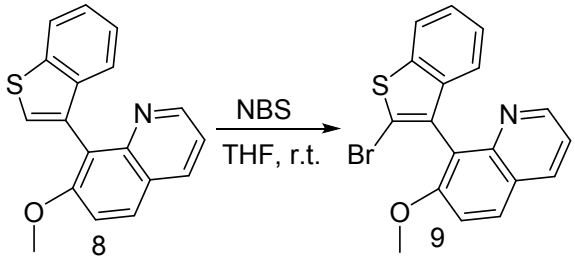


500 mL 3-neck flask was charged with benzo[*b*]thiophene boronic acid (1.64 g, 9.21 mmol), compound **2** (1.46 g, 6.15 mmol), Na_2CO_3 (0.98 g, 9.24 mmol), water (75 mL) and dimethoxyethene (150 mL). After degased for 30 min $Pd(PPh_3)_4$ was added to the mixture and then the mixture was heated up to 75-85 °C and keep at this temperature for 24 h (monitored by TLC analysis). After the reaction the mixture was cooled to room temperature and water was added to mixture. Then the mixture was extracted with ethyl acetate. The organic layer was dried with anhydrous magnesium sulfate and the crude product was purified by silica gel chromatography (hexane/EtOAc = 3:1) to get compound **8** (1.61 g, 90 %) as brown solid.

^{1}H-NMR (300 MHz, TMS, $CDCl_3$) δ: 3.85 (s, 3H), 7.23-7.34 (m, 4H), 7.48(s, 1H), 7.50-7.51 (d, 1H, *J* = 3 Hz), 7.91-7.94 (d, 2H, *J* = 9 Hz), 8.14-8.18 (d, 1H, *J* = 12 Hz), 8.80-8.82 (d, 1H, *J* = 6 Hz).

EI-HRMS: calcd for $C_{18}H_{13}NOS^+$ $[M]^+$ 291.0718; found 291.0705.

Synthesis of 8-(2-bromobenzo[*b*]thiophen-3-yl)-7-methoxyquinoline **(9)**

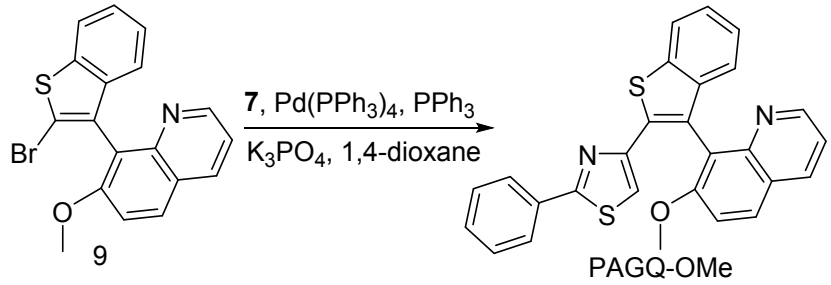


100 mL 2-neck flask was charged with compound **8** (1.45 g, 4.97 mmol), NBS (2.3 g, 12.92 mmol) and 30 mL THF. The mixture was stirred at 0 °C a while and then attired at room temperature for overnight (monitored by TLC analysis) under argon gas atmosphere. After the reaction, water was added to mixture. Then the mixture was extracted with ethyl acetate. The organic layer was dried with anhydrous magnesium sulfate and the crude product was purified by silica gel chromatography (hexane/EtOAc = 4:1) to get compound **9** (1.3 g, 71 %) as brown solid.

^{1}H-NMR (300 MHz, TMS, $CDCl_3$) δ: 3.89 (s, 3H), 7.05-7.08 (d, 1H, *J* = 9 Hz), 7.15-7.21 (t, 1H, *J* = 9 Hz), 7.26-7.32 (m, 2H), 7.49-7.52 (d, 2H, *J* = 9 Hz), 7.77-7.80 (d, 1H, *J* = 9 Hz), 7.96-7.99 (d, 1H, *J* = 9 Hz), 8.16-8.19 (d, 1H, *J* = 9 Hz), 8.80-8.82 (d, 1H, *J* = 6 Hz).

ESI-HRMS: calcd for $C_{18}H_{13}BrNOS^+$ $[M+H]^+$ 369.99012; found 369.99044.

Synthesis of 4-(3-(7-methoxyquinolin-8-yl)benzo[*b*]thiophen-2-yl)-2-phenylthiazole **(PAGQ-OMe)**



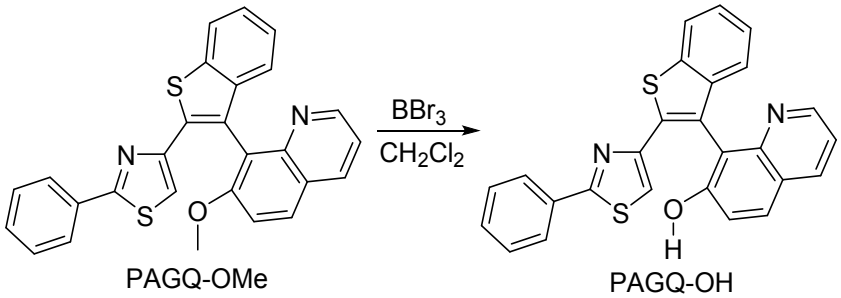
300 mL 3-neck flask was charged with 8-(2-bromobenzo[*b*]thiophen-3-yl)-7-methoxy-quinoline (1.3 g, 3.5 mmol), compound **7**, 2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiazole (1.878 g, 6.54 mmol), PPh_3 (0.468 g, 1.79 mmol), K_3PO_4 aq. (2 M, 30 mL), and 1,4-dioxane (80 mL). The mixture was degassed by using argon gas for 30 min. Then $Pd(PPh_3)_4$ was added to the mixture and the heated up to 110 °C for 24 h. After the reaction the mixture was cool to room temperature. Then some water was added to the mixture and the mixture was extracted with AcOEt. The organic layer was dried with anhydrous $MgSO_4$. After the solvent was evaporated, the crude product was purified with silica-gel column chromatography (hexane/EtOAc = 4:1) to afford compound **PAGQ-OMe** (0.66 g, 42 %) as light yellow solid.

^{1}H-NMR (300 MHz, TMS, $CDCl_3$) δ: 3.76 (s, 3H), 6.35 (s, 1H), 7.04-7.07 (d, 1H, J = 9 Hz), 7.16-7.22 (t, 1H, J = 18 Hz), 7.22-7.34 (m, 4H), 7.39-7.42 (m, 3H), 7.51-7.54 (d, 1H, J = 9 Hz), 7.88-7.93 (m, 1H), 8.00-8.03 (d, 1H, J = 9 Hz), 8.18-8.21 (d, 1H, J = 9 Hz), 8.75-8.77 (d, 1H, J = 6 Hz).

^{13}C-NMR (300 MHz, TMS, $CDCl_3$) δ: 166.42, 158.45, 151.81, 150.78, 148.42, 141.75, 139.27, 136.11, 135.37, 133.56, 130.16, 129.94, 129.00, 127.70, 126.78, 124.61, 124.17, 124.00, 123.38, 122.52, 120.40, 119.45, 114.70, 113.50, 56.81.

ESI-HRMS: calcd for $C_{27}H_{18}N_2OS_2^+$ $[M+H]^+$ 451.09388; found 451.09339.

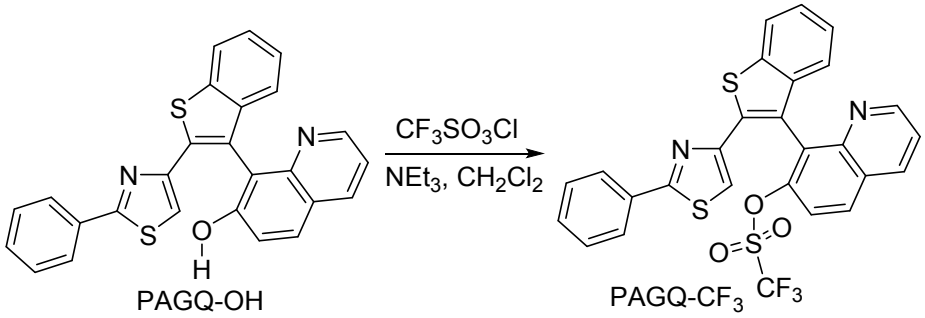
Synthesis of 8-(2-(2-phenylthiazol-4-yl)benzo[*b*]thiophen-3-yl)quinolin-7-ol **(PAGQ-OH)**



20 mL 2-neck flask was charged with compound **PAGQ-OMe**(150 mg, 0.33 mmol) and CH_2Cl_2 (8 mL) under argon gas atmosphere. After the flask was covered with aluminium

foil, BBr_3 (1.7 mL, 1.65 mmol) was added to the mixture dropwise. Then the mixture was stirred at room temperature for 3 days (monitored by TLC analysis). Then brine was added to the mixture and extracted with CH_2Cl_2. The organic layer was dried with anhydrous magnesium sulfate. After the solvent was removed, the crude product **PAGQ-OH** was used directly without any purification.

Synthesis of 8-(2-(2-phenylthiazol-4-yl)benzo[*b*]thiophen-3-yl)quinolin-7-yl trifluoro-methanesulfonate **(PAGQ-CF_3)**



20 mL 2-neck flask was charged with crude compound **PAGQ-OH**, and CH_2Cl_2 (10 mL) under argon gas atmosphere. Then the mixture was cooled to 0 °C, and NEt_3 (0.5 mL), trifluoro-methanesulfonyl chloride (0.26 mL, 1.0 mmol) were added to the solution in sequence. Then the mixture was stirred at 0 °C for 3 h. After the reaction, the mixture was extracted with brine and CH_2Cl_2 and the organic layer was dried with anhydrous magnesium sulfate. After the solvent removed, the crude product was purified by silica gel chromatography (hexane/EtOAc = 4:1). The final compound was further purified by reverse phase HPLC by using acetonitrile as eluent to afford compound **PAGQ-CF_3** (50 mg, 34 %) as light yellow solid.

^{1}H-NMR (300 MHz, TMS, $CDCl_3$) δ: 6.22 (s, 1H), 6.67 (s, 1H), 7.04-7.07 (d, 1H, J = 9 Hz), 7.20-7.23 (t, 1H, J = 9 Hz), 7.35-7.38 (d, 1H, J = 9 Hz), 7.42-7.47 (m, 4H), 7. 91-7.96 (m, 4H), 8.17-8.20 (d, 1H, J = 9 Hz), 8.73-8.75 (d, 1H, J = 6 Hz).

^{13}C-NMR (300 MHz, TMS, $CDCl_3$) δ: 167.51, 155.29, 151.37, 149.45, 148.53, 141.08, 139.65, 136.28, 133.17, 130.61, 130.14, 129.15, 126.83, 125.42, 124.78, 124.10, 123.80, 122.62, 119.41, 119.32, 116.89, 115.31.

ESI-HRMS: calcd for $C_{27}H_{18}N_2OS_2Na^+$ $[M+Na]^+$ 591.00946; found 591.00920.

1.1.3 Photolithography study of SU-8

The photolithography was performed on the glass slide. To increase the adhesion strength, the slide was previously washed with ethanol/acetone solution (*v*/*v* = 1:1, filtered 10 times with syringe filter HP020AN which bore diameter is 0.20 μm).

Diethyl glycol diethyl ether (DGDE) was used as solvent which can dissolve the PAG very well. The concentration of SU-8 in the solvent is 25 wt % and the PAG is 10 wt % relative to the SU-8. SU-8 films were prepared by spin-coating of the mixture of SU-8 and PAG on glass slides (600rpm/s for 20s) by using a spin coater. The spin-coated film on the glass slide was soft baked on a hotplate at 65 ºC for 3 min followed by second bake at 90 ºC for 7 min to remove the excess solvent. Then the film was exposed to the UV light (λ=365 nm, 22mW cm^{-2}) with a photomask for 20 min and post-baked at 65 ºC for 3 min and 90 ºC for 2 min. After slowly cooling to the room temperature, the SU-8 sample was developed in SU-8 developer for 1 min and rinsed with isopropanol, and dried with blowing nitrogen. The image was detected with SEM.

1.1.4 Photoinduced Cationic Polymerization of propylene oxide

The sample tube was charged with propylene oxide monomer and photoacid generator **PAGQ-CF_3** (0.2 mol%) sealed with rubber septum, and then degassed with argon gas prior to irradiation. After the deaerated sample was irradiated upon UV light for a given time, the mixture was diluted with $CHCl_3$ and characterized with MALDI-MS. A series of mass peaks with the interval in m/z of 58 clearly demonstrated the successful progress of photoinduced cationic polymerization of propylene oxide by the newly developed **PAGQ-CF_3**.

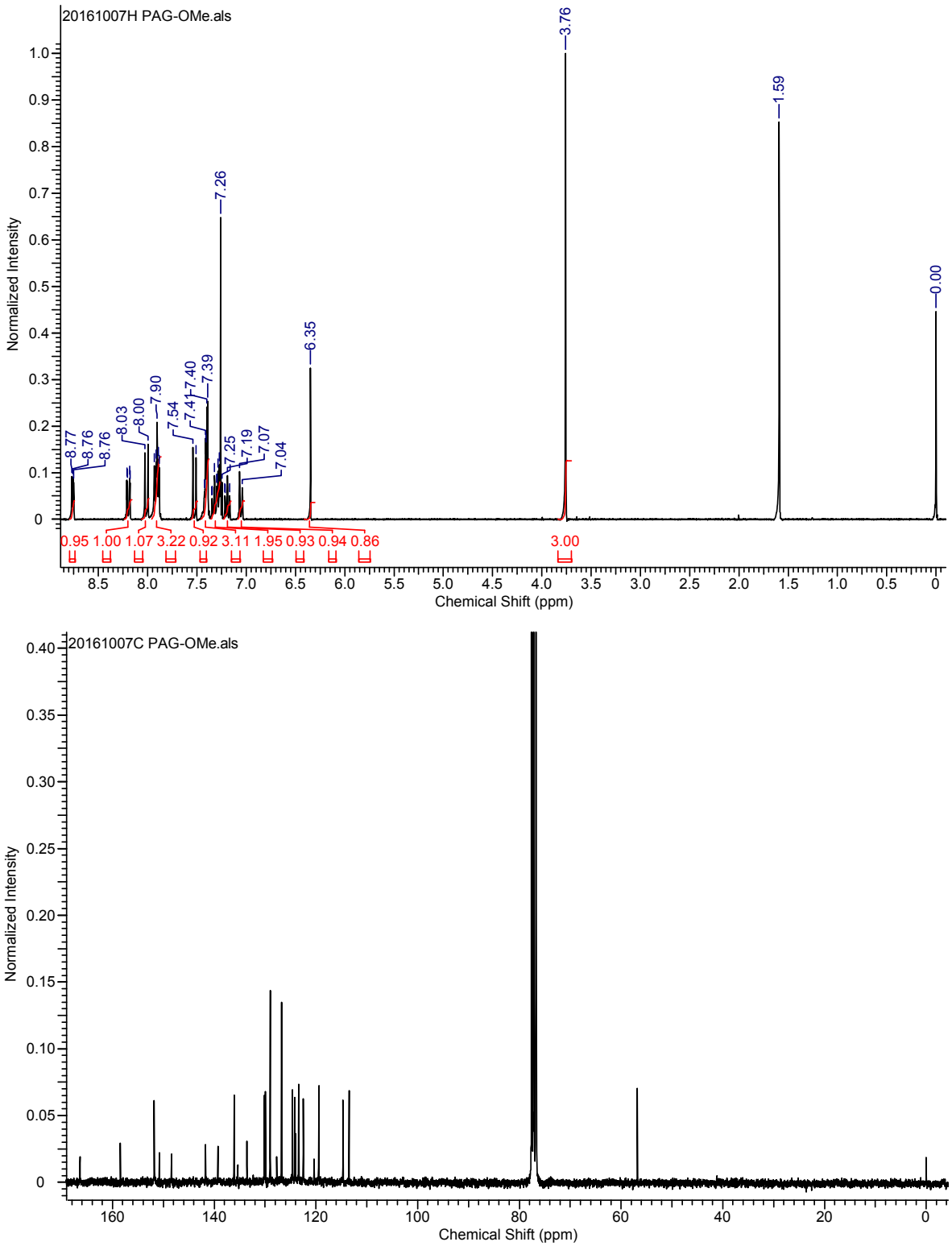


Figure S1. ^{1}H and ^{13}C-NMR of compound **PAGQ-OMe** in $CDCl_3$.

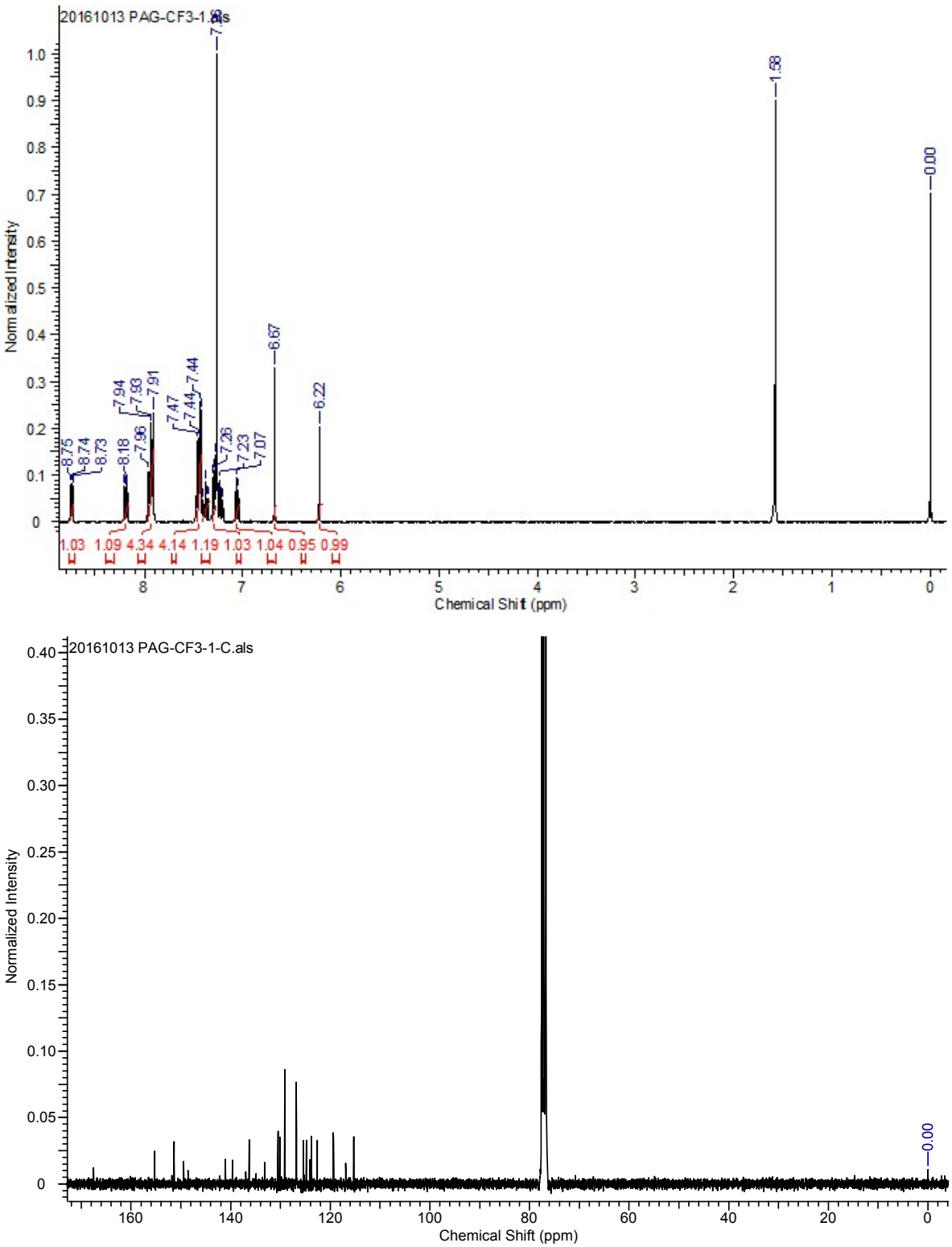
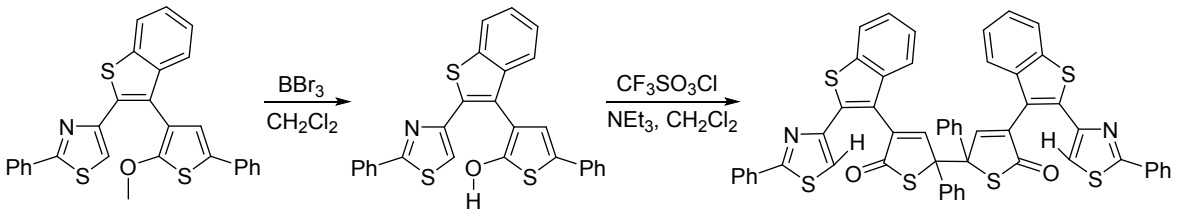
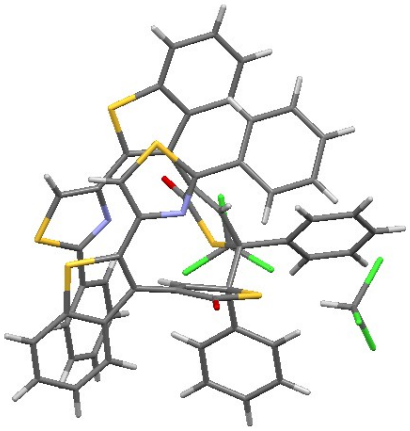


Figure S2. ^{1}H and ^{13}C-NMR of compound **PAGQ-CF$_3$** in $CDCl_3$.

1.2 Trial to introduce trifluoromethanesulfonyl acid



Scheme S2. Dimeric structure was prepared from the identical procedure according to **PAGQ-CF$_3$**. This dimeric structure was confirmed by mass spectrum and X-ray analysis.[2]



ESI-HRMS: calcd for $C_{54}H_{32}N_2O_2S_6$ 932.07880; found 932.07889.

Figure S3. ORTEP drawing of the dimeric compound, showing 50% probability displacement ellipsoids. Gray: carbon, yellow: sulfur, blue: nitrogen.

Table S1. Crystallographic parameters and refinement details for dimeric structure.

formula	$C_{54}H_{32}N_2O_2S_6$	V(Å^3)	5178.32(19)
formula weight	933.22	Z	4
crystal system	Monoclinic	ρ (gcm^3)	1.503
space group	$P2_1/c$ (#14)	T (K)	123
a (Å)	13.2024(3)	refl. measured	70934
b (Å)	13.1341(3)	refl. unique	9471
c (Å)	29.9533(19)	R_1 (I>2σ(I))	0.0906
α (deg)		wR_2 (all data)	0.2542
β (deg)	64.445(7)		
γ (deg)		CCDC No.	CCDC 1528071

1.3 Photoreaction of PAGQ-OMe

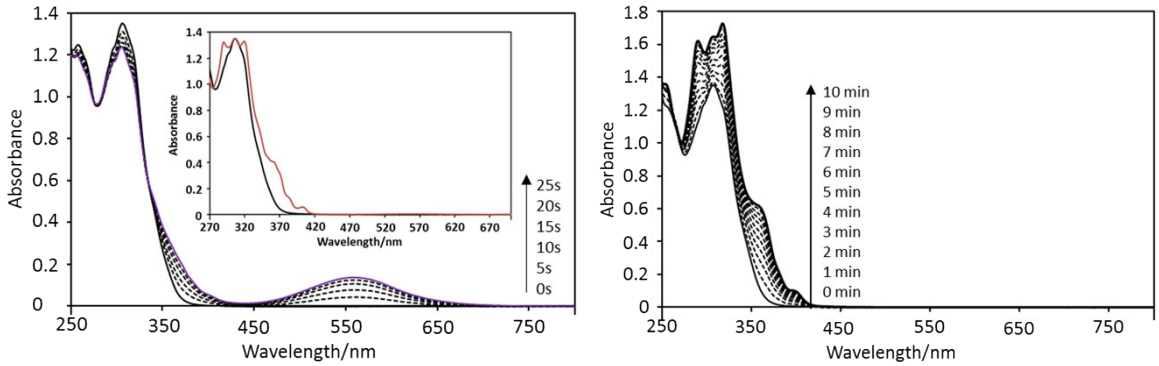


Figure S4. Absorption spectral change of **PAGQ-OMe** upon UV (313 nm) irradiation in hexane (c = 5.1 × 10^{-5} M, left. Inset: keep in dark for 30 min after 30 s irradiation) and in methanol (c = 4.9 ×10^{-5}M, right).

1.4 Photoreaction of PAGQ-CF_3

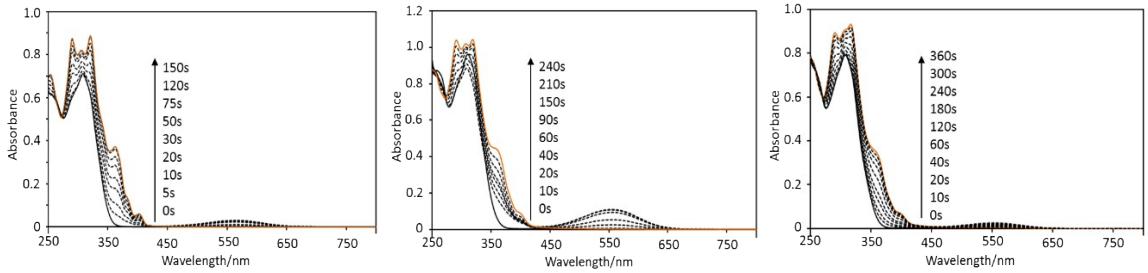


Figure S5. UV-Vis absorption spectral change of **PAGQ-CF_3** in hexane (c = 1.98 × 10^{-5} M, left), $CHCl_3$ (c = 2.56 × 10^{-5} M, middle) and in methanol (c = 2.20 × 10^{-5} M, right) upon UV irradiation (λ = 313 nm).

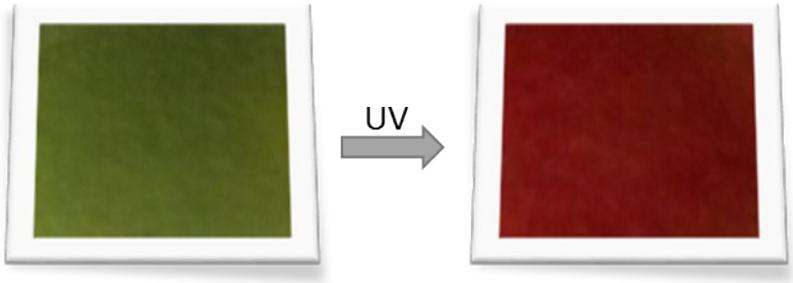


Figure S6. Acid elimination reaction detected by pH paper.
(Left: pH paper wetted by **PAGQ-CF_3** acetonitrile solution without UV irradiation; Right: color change of pH paper after UV irradiation.)

1.5 Acid Releasing Process of PAGQ-CF_3(CF) After UV Irradiation

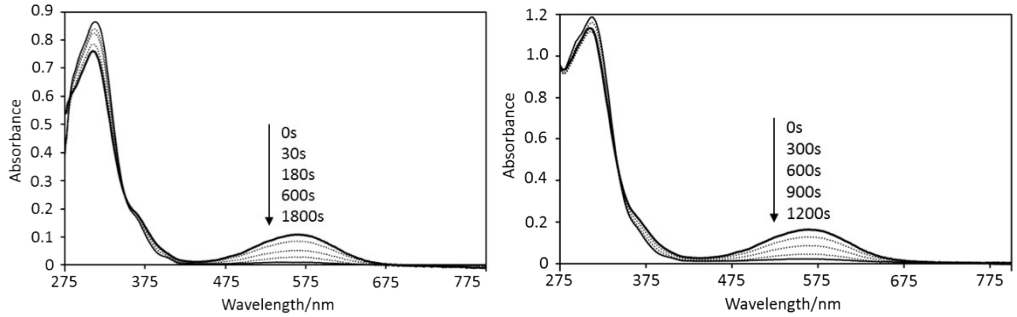


Figure S7. Absorption spectral changes of **PAGQ-CF_3** after one minute UV irradiation (λ = 313 nm) in toluene (c = 1.91 × 10^{-5} M, left) and in $CHCl_3$ (c = 2.21 × 10^{-5} M, right).

1.6 Photoreaction of PAGQ-CF_3 at High Temperature

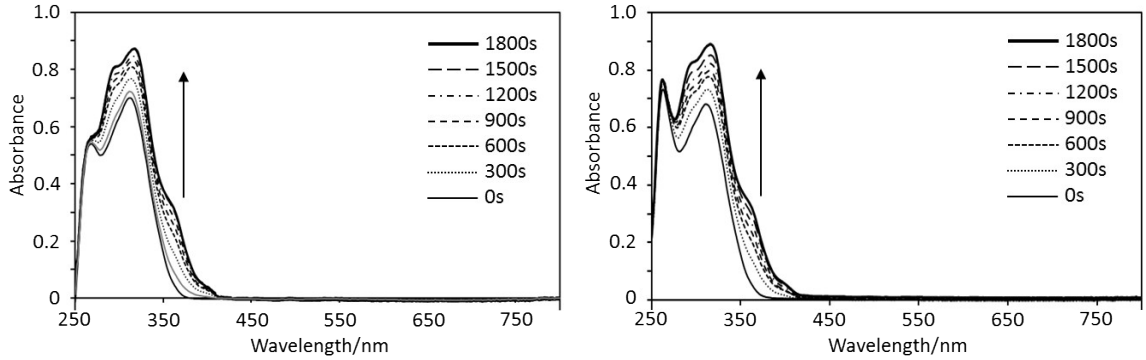


Figure S8. UV-Vis absorption spectral change of **PAGQ-CF_3** in DMSO (c = 2.04 × 10^{-5} M) upon UV irradiation (λ = 313 nm) at 60 °C (left) and 90 °C (right);

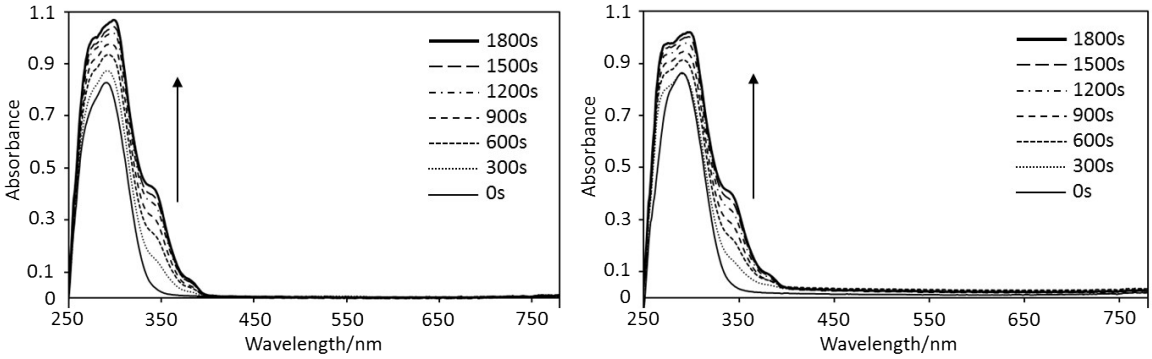


Figure S9. UV-Vis absorption spectral change of **PAGQ-CF_3** in toluene (c = 2.45 × 10^{-5} M) upon UV irradiation (λ = 313 nm) at 60 °C (left) and 90 °C (right);

1.7 Absorption Spectral Change of 1c

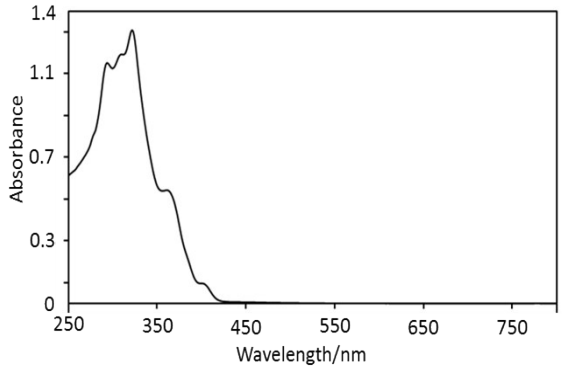


Figure S10. UV-Vis absorption spectral change of **1c** in toluene.

1.8 Degradation Process of PAGQ-CF_3(CF).

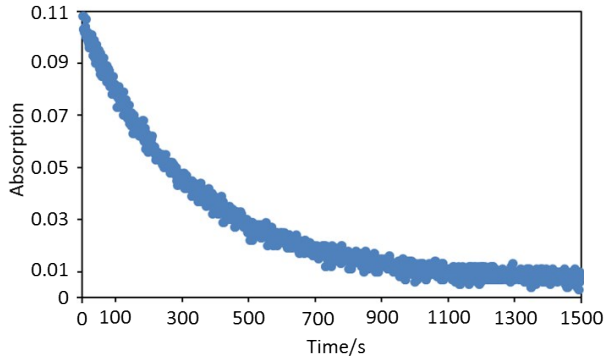


Figure S11. Absorption degradation tendency of **PAGQ-CF_3(CF)** at 564 nm after one minute UV irradiation (λ = 313 nm) in toluene.

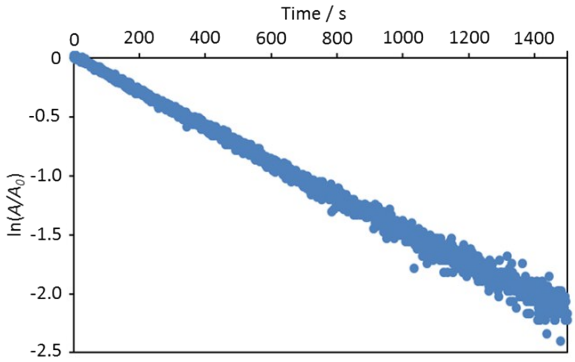


Figure S12. Decay line of peak absorbance (564 nm) by acid releasing process from **PAGQ-CF_3(CF)** in toluene.

1.9 X-ray Crystallography Analysis of 1c.

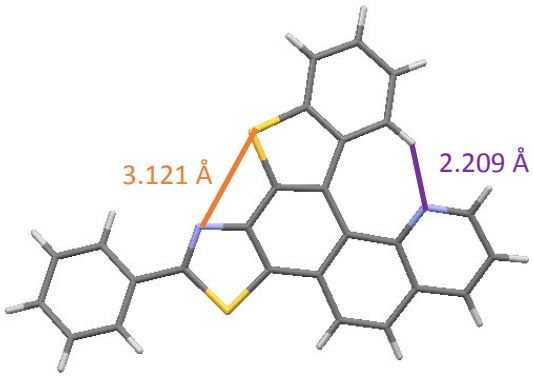


Figure S13. ORTEP drawing of **1c**, showing 50% probability displacement ellipsoids. Gray: carbon, yellow: sulfur, blue: nitrogen.

Table S2. Crystallographic parameters and refinement details for **1c**.

formula	$C_{26}H_{14}N_2S_2$	V(Å3)	1847.65(7)
formula weight	418.53	Z	4
crystal system	Monoclinic	ρ (gcm^3)	1.504
space group	$P2_1/c$ (#14)	T (K)	123
a (Å)	11.6887(2)	refl. measured	25095
b (Å)	16.7383(3)	refl. unique	3381
c (Å)	9.49897(18)	R_1 (I>2σ(I))	0.0334
α (deg)		wR_2 (all data)	0.0851
β (deg)	96.182(7)		
γ (deg)		CCDC No.	CCDC 1523529

2.0 DFT Calculation

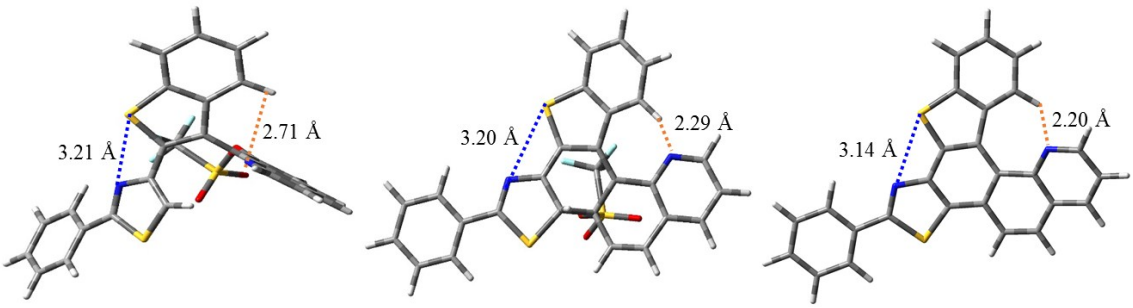


Figure S14. Optimized structures of **PAGQ-CF$_3$**, **PAGQ-CF$_3$(CF)** and **1c** by DFT method with ωB97XD/6-31G(d) functional and (dashed line is non-covalent interactions).

2.1 Quantum Yields and Photophysical Properties of PAGQ-OMe, PAGQ-CF_3 and 1c

Table S3. Photophysical properties of **PAGQ-OMe**, **PAGQ-CF_3** and **1c**.

Compd.	λ_{Abs} / nm ($\varepsilon \times 10^{-4}$ / $M^{-1}cm^{-1}$)	Φ^d
PAGQ-OMe	310 (5.28),[a] 309 (5.64),[b] 307 (5.96)[c]	0.61,[a] 0.52,[b] 0.47[c]
PAGQ-CF_3	311 (6.86),[a] 310 (7.00)[b], 309 (7.10)[c]	0.47,[a] 0.41,[b] 0.36[c]
1c	294 (5.52),[a] 310 (5.62),[a] 322 (6.06),[a] 361 (2.59),[a] 402 (0.48),[a] 293 (6.18),[b] 308 (6.19),[b] 321 (6.68),[b] 360 (2.98),[b] 402 (0.54),[b]	–

[a] Measured in toluene; [b] in chloroform; [c] in methanol;

[d] Apparent quantum yield for ring-cyclization reaction of **PAGQ-OMe** and for the photoacid generation of **PAGQ-CF_3**.

2.2 ^{1}H-NMR Study of PAGQ-CF_3 with UV Irradiation

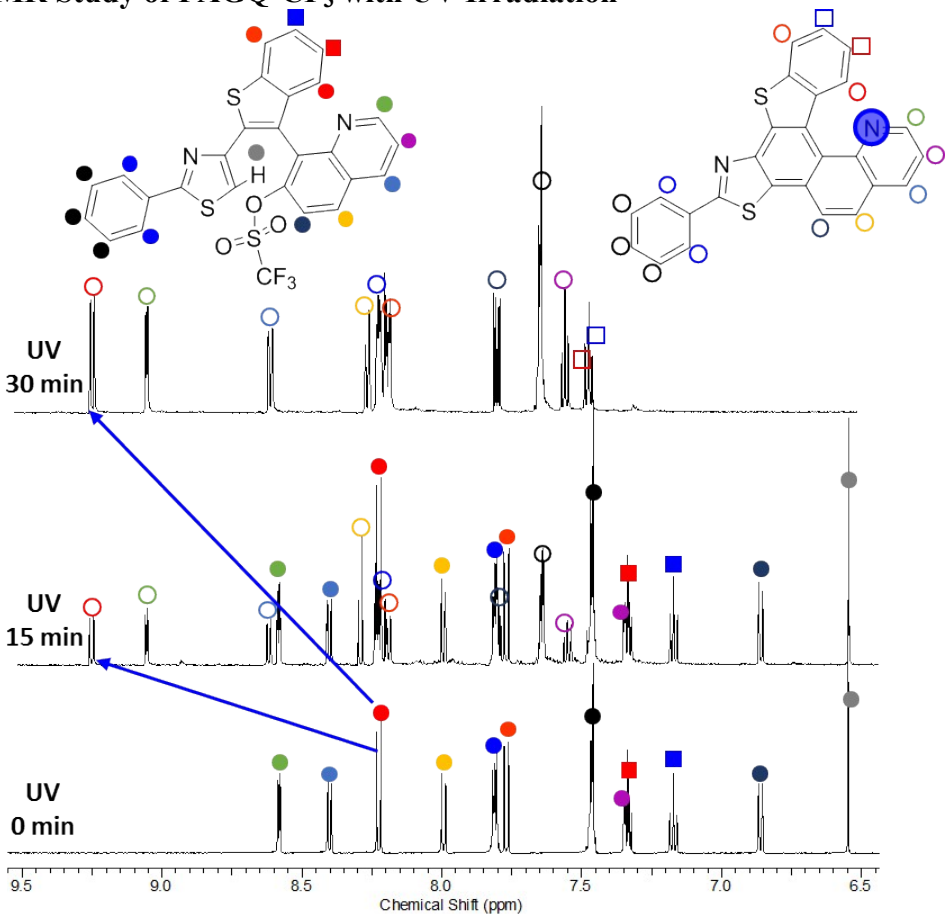


Figure S15. ^{1}H-NMR spectral change of **PAGQ-CF_3** with UV irradiation in DMSO-d_6. (For these ^{1}H-NMR measurements, the acid could be released from the **PAGQ-CF_3(CF)** immediately in DMSO at r.t., thus **PAGQ-CF_3(CF)** could not be detected by ^{1}H-NMR.)

2.3 MALDI-MS Spectra of Polymeri

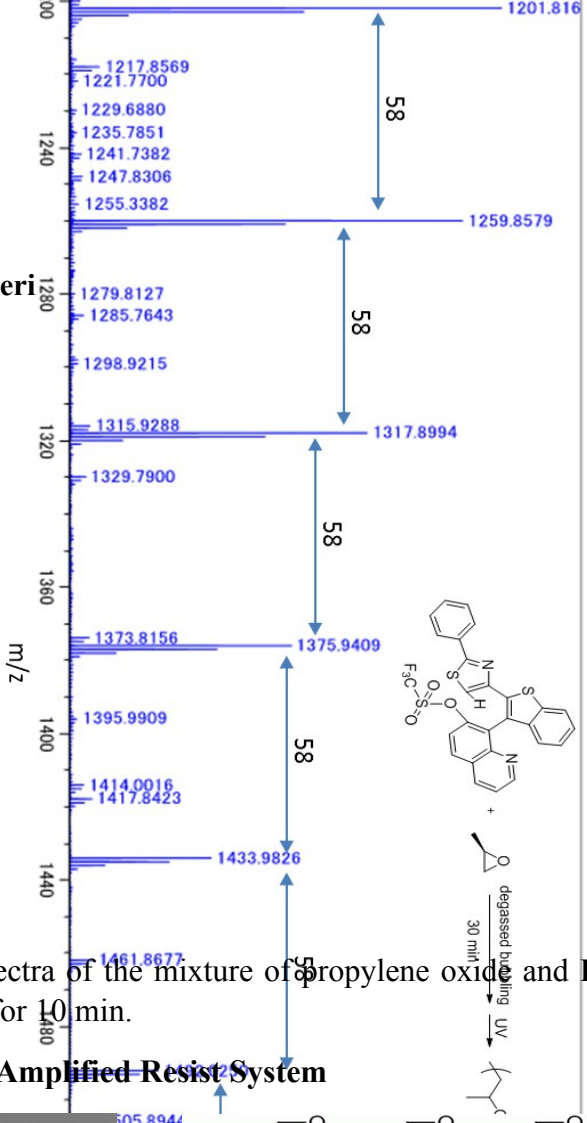


Figure S16. MALDI-TOF-MS spectra of the mixture of propylene oxide and **PAGQ-CF$_3$** (0.2 mol%) after UV irradiadtion for 10 min.

2.4 Application in a Chemically Amplified Resist System

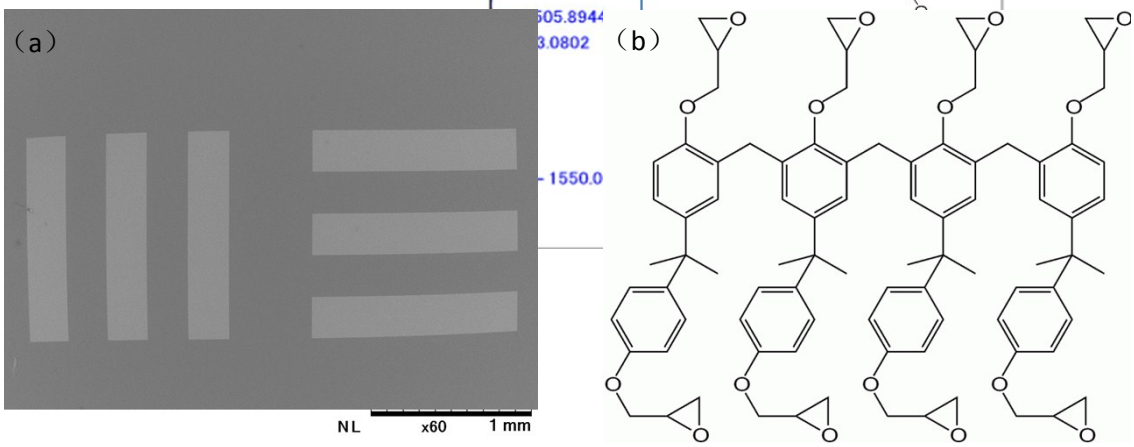


Figure. S17. SEM image (a) of a photopattern fabricated by a chemically amplified photo-resist system containing **PAGQ-CF$_3$** and SU-8 (b).

2.5 Reference:

[1] T. Sumi, Y. Takagi, A. Yagi, M. Morimoto and M. Irie, *Chem. Commun.*, 2014, **50**, 3928-3930.
[2] R. Li, T. Nakashima, R. Kanazawa, O. Galangau and T. Kawai, *Chem. Eur. J.*, 2016, **22**, 16250-16257.

[3] T. Nakashima, K. Tsuchie, R. Kanazawa, R. Li, S. Iijima, O. Galangau, H. Nakagawa, K. Mutoh, Y. Kobayashi, J. Abe and T. Kawai, *J. Am. Chem. Soc.*, 2015, **137**, 7023-7026.