Supporting Information for

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

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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 ($\lambda$ = 313 nm).

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)

\[
\begin{align*}
\text{O} & \quad \text{NH}_2 \\
\text{FeSO}_4 \cdot 7\text{H}_2\text{O}, \text{CH}_3\text{SO}_3\text{H} & \quad \text{Glycerol} \\
\rightarrow & \quad \text{O} \quad \text{N} \\
\end{align*}
\]

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\(_4\)·H\(_2\)O (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\(_3\)) \(\delta\): 3.96 (s, 3H), 7.19-7.29 (m, 2H), 7.43(sd, 1H), 7.68-7.71 (d, 1H, \(J = 9 \text{ Hz}\)), 8.06-8.09 (d, 1H, \(J = 9 \text{ Hz}\)), 8.83-8.85 (d, 1H, \(J = 9 \text{ Hz}\)).

ESI-HRMS: calcd for C\(_{10}\)H\(_{10}\)NO\(^+\) [M+H]\(^+\) 160.07624; found 160.07621.

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

\[
\begin{align*}
\text{O} & \quad \text{N} \\
\text{CH}_2\text{Cl}_2 & \quad \text{Br} \\
\rightarrow & \quad \text{O} \\
\end{align*}
\]

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\(_2\)S\(_2\)O\(_3\) 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\(_3\)) \(\delta\): 4.09 (s, 3H), 7.33-7.39 (m, 2H), 7.81-7.84 (d, 1H, \(J = 9 \text{ Hz}\)), 8.12-8.15 (d, 1H, \(J = 9 \text{ Hz}\)), 9.03-9.04 (d, 1H, \(J = 3 \text{ Hz}\)).

EI-HRMS: calcd for C\(_{10}\)H\(_8\)BrNO\(^+\) [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), Na₂CO₃ (0.98 g, 9.24 mmol), water (75 mL) and dimethoxyethene (150 mL). After degased for 30 min Pd(PPh₃)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.

¹H-NMR (300 MHz, TMS, CDCl₃) 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).


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.

¹H-NMR (300 MHz, TMS, CDCl₃) 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).

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-methoxyquinoline (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), PPh₃ (0.468 g, 1.79 mmol), K₃PO₄ aq. (2 M, 30 mL), and 1,4-dioxane (80 mL). The mixture was degassed by using argon gas for 30 min. Then Pd(PPh₃)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 MgSO₄. 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.

1H-NMR (300 MHz, TMS, CDCl₃) 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).

13C-NMR (300 MHz, TMS, CDCl₃) 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.


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 CH₂Cl₂ (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$_2$Cl$_2$. 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 trifluoromethanesulfonate (PAGQ-CF$_3$)

![Chemical structure of PAGQ-CF$_3$]

20 mL 2-neck flask was charged with crude compound PAGQ-OH, and CH$_2$Cl$_2$ (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$_2$Cl$_2$ 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$_2$OS$_2$Na$^+$ [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 cm²) 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-CF₃ (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 CHCl₃ 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-CF₃.
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$_2$O$_2$S$_6$ 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.

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<td>$\gamma$ (deg)</td>
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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-CF₃

Figure S5. UV-Vis absorption spectral change of PAGQ-CF₃ in hexane (c = 1.98 × 10^{-5} M, left), CHCl₃ (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-CF₃ 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-CF₃(CF).

Figure S11. Absorption degradation tendency of PAGQ-CF₃(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-CF₃(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.

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<th>Value</th>
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2.0 DFT Calculation

Figure S14. Optimized structures of PAGQ-CF_3, PAGQ-CF_3(CF) and 1c by DFT method with oB97XD/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.

<table>
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<th>Compd.</th>
<th>$\lambda_{Abs} / \text{nm}$ ($\varepsilon \times 10^{-4} / \text{M}^{-1} \text{cm}^{-1}$)</th>
<th>$\Phi^{d}$</th>
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</thead>
<tbody>
<tr>
<td>PAGQ-OMe</td>
<td>310 (5.28),$^a$ 309 (5.64),$^b$ 307 (5.96)$^c$</td>
<td>0.61,$^a$ 0.52,$^b$ 0.47$^c$</td>
</tr>
<tr>
<td>PAGQ-CF$_3$</td>
<td>311 (6.86),$^a$ 310 (7.00)$^b$, 309 (7.10)$^c$</td>
<td>0.47,$^a$ 0.41,$^b$ 0.36$^c$</td>
</tr>
<tr>
<td>1c</td>
<td>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),$^b$</td>
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</table>

[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 Polymerized Propylene Oxide

Figure S16. MALDI-TOF-MS spectra of the mixture of propylene oxide and PAGQ-CF$_3$ (0.2 mol%) after UV irradiation 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: