Supporting Information

A Scalable and Efficient Approach to High-Fidelity Amine Functionalized Poly(ethylene glycol) Derivatives

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1. **Materials**

Poly(ethylene glycol) derivatives, triethylamine (TEA), methanesulfonyl chloride (MsCl), bis(tert-butoxycarbonyl)amine ((Boc)$_2$NH), $N,N$-Dimethylformamide (DMF), tetrahydrofuran (THF), acetonitrile (CH$_3$CN), $1,4$-dioxane, Pd/C, tert-butanol ($t$-BuOH), potassium $t$-butoxide ($t$-BuOK), 3-bromopropyne, sodium hydride (NaH), ferric chloride (FeCl$_3$), acetic anhydride and sodium hydroxide (NaOH) are purchased from Energy Chemical and used as received unless otherwise stated.

2. **Characterization**

$^1$H NMR spectra and $^{13}$C NMR were recorded on a Bruker AV-400 spectrometer. MALDI-TOF Mass was performed on a Bruker Autoflex III mass spectrometer in linear or reflected positive ion mode. The matrix was trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB), and the solvent was CH$_2$Cl$_2$. Number-average molecular weights ($M_n$) and polydispersity indexes (PDI) were determined by Size Exclusion Chromatography (SEC) on a Waters 1515 HPLC pump equipped with Waters 2414 Refractive index Detector (eluent: DMF; flow rate: 1.0 mL/min; temperature: 80 °C; injection volume: 100.0 μL standard: polystyrene in the molecular weight range from 660 to 1.97×10$^5$ Da).

3. **Typical procedures for the synthesis of PEG-NH$_2$s**

3.1 **Typical procedure for the synthesis of PEG-OMss**

PEG-OH (20g, 1.0 eq) was dissolved with anhydrous dichloromethane (150 mL) in a round-bottomed flask followed by the addition of triethylamine (2 eq). The solution was then stirred at 0°C for 15min. MsCl (1.2 eq) was dissolved in anhydrous dichloromethane (50 mL) and added dropwise to the solution. The resulting mixture was stirred at room temperature overnight. The solution was quenched by water, and extracted with dichloromethane for three times. The combined organic layer was dried with anhydrous Na$_2$SO$_4$, filtered, concentrated, precipitated with diethyl ether and dried in vacuum.
mPEG_{23}-OMs (1a), white solid, 18.8g, 87.2% yield. {\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 4.38 (t, \(J = 4.0\) Hz, 2H), 3.85-3.50 (m, 89H), 3.38 (s, 3H), 3.09 (s, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\): 71.86, 70.50, 69.28, 68.95, 58.94, 37.65.}

mPEG_{45}-OMs (1b), white solid, 19.2g, 92.4% yield. {\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 4.38 (t, \(J = 4.0\) Hz, 2H), 3.85-3.50 (m, 180H), 3.38 (s, 3H), 3.09 (s, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\): 71.92, 70.56, 69.31, 69.00, 59.00, 37.71.}

mPEG_{114}-OMs (1c), white solid, 19.5g, 96.0% yield. {\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 4.38 (t, \(J = 4.0\) Hz, 2H), 3.85-3.50 (m, 453H), 3.38 (s, 3H), 3.09 (s, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\): 71.89, 70.53, 69.27, 68.97, 58.97, 37.68.}

mPEG_{233}-OMs (1d), white solid, 19.6g, 97.2% yield. {\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 4.38 (t, \(J = 4.0\) Hz, 2H), 3.85-3.50 (m, 928H), 3.37 (s, 3H), 3.07 (s, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\): 71.90, 70.54, 69.29, 68.99, 59.98, 37.70.}

mPEG_{485}-OMs (1e), white solid, 19.5g, 97.1% yield. {\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 4.38 (t, \(J = 4.0\) Hz, 2H), 3.85-3.55 (m, 1937H), 3.38 (s, 3H), 3.08 (s, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\): 72.04, 70.68, 69.39, 69.12, 59.13, 37.84.}

mPEG_{909}-OMs (1f), white solid, 19.0g, 94.8% yield. {\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 4.38 (t, \(J = 4.0\) Hz, 2H), 3.85-3.55 (m, 3634H), 3.38 (s, 3H), 3.08 (s, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\): 72.04, 70.68, 69.39, 69.12, 59.13, 37.84.}

MsO-PEG_{23}-OMs (1h), white solid, 19.0g, 94.8% yield. {\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 4.38 (t, \(J = 4.0\) Hz, 2H), 3.85-3.55 (m, 2725H), 3.38 (s, 3H), 3.07 (s, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\): 70.53, 69.29, 68.97, 58.75, 37.45.}

MsO-PEG_{45}-OMs (1i), white solid, 18.7g, 86.7% yield. {\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 4.38 (t, \(J = 4.0\) Hz, 2H), 3.85-3.55 (m, 178H), 3.38 (s, 3H), 3.09 (s, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\): 70.54, 69.09, 68.77, 58.75, 37.45.}

MsO-PEG_{77}-OMs (1j), white solid, 19.0g, 90.8% yield. {\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 4.38 (t, \(J = 4.0\) Hz, 2H), 3.85-3.55 (m, 305H), 3.38 (s, 3H), 3.09 (s, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\): 70.52, 69.28, 68.97, 37.68.
MsO-PEG\textsubscript{150}-OMs (1k), white solid, 19.0g, 92.8% yield. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 4.38 (t, \(J = 4.0\) Hz, 4H), 3.85-3.50 (m, 596H), 3.08 (s, 6H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\): 70.54, 69.29, 68.99, 37.70.

MsO-PEG\textsubscript{182}-OMs (1l), white solid, 19.3g, 94.6% yield. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 4.38 (t, \(J = 4.0\) Hz, 4H), 3.85-3.50 (m, 723H), 3.08 (s, 6H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\): 70.53, 69.28, 68.98, 37.69.

MsO-PEG\textsubscript{227}-OMs (1m), white solid, 19.5g, 96.0% yield. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 4.38 (t, \(J = 4.0\) Hz, 4H), 3.85-3.50 (m, 905H), 3.08 (s, 6H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\): 70.55, 69.29, 69.00, 37.71.

MsO-PEG\textsubscript{455}-OMs (1n), white solid, 19.5g, 96.7% yield. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 4.38 (t, \(J = 4.0\) Hz, 4H), 3.85-3.55 (m, 3178H), 3.08 (s, 6H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\): 70.54, 69.29, 68.99, 37.69.

MsO-PEG\textsubscript{795}-OMs (1o), white solid, 19.5g, 97.1% yield. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 4.38 (t, \(J = 4.0\) Hz, 4H), 3.80-3.55 (m, 3178H), 3.08 (s, 6H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\): 70.54, 69.29, 68.99, 37.69.

4-ARM-PEG\textsubscript{227}-OMs (1p), white solid, 19.3g, 93.5% yield. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 4.38 (t, \(J = 4.0\) Hz, 8H), 3.85-3.49 (m, 901H), 3.09 (s, 12H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\): 70.96, 70.56, 70.01, 69.31, 69.01, 37.72.

4-ARM-PEG\textsubscript{455}-OMs (1q), white solid, 19.5g, 96% yield. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 4.38 (t, \(J = 4.0\) Hz, 8H), 3.85-3.50 (m, 1810H), 3.08 (s, 12H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\): 70.98, 70.59, 70.04, 69.32, 69.04, 37.74.

8-ARM-PEG\textsubscript{227}-OMs (1r), white solid, 19.2g, 90.2% yield. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 4.38 (t, \(J = 4.0\) Hz, 16H), 4.10-3.40 (m, 893H), 3.09 (s, 24H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\): 71.41, 70.54, 69.78, 69.31, 68.99, 37.70.

8-ARM-PEG\textsubscript{455}-OMs (1s), white solid, 19.5g, 94.5% yield. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 4.38 (t, \(J = 4.0\) Hz, 16H), 3.85-3.50 (m, 1802H), 3.08 (s, 24H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\): 71.40, 70.54, 69.78, 69.29, 68.99, 37.70.

8-ARM-PEG\textsubscript{795}-OMs (1t), white solid, 19.5g, 96% yield. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 4.38 (t, \(J = 4.0\) Hz, 16H), 3.85-3.50 (m, 3620H), 3.08 (s, 24H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\): 71.36, 70.59, 69.82, 69.33, 69.03, 37.74.
3.2 Typical procedure for the synthesis of PEG-N(Boc)$_2$S

PEG-OMs (I) (10g, 1.0 eq) was dissolved with anhydrous acetonitrile (100 mL) in a round-bottomed flask. Then, $t$-BuOK (3.0 eq) and (Boc)$_2$NH (3.0 eq) were added to the solution. The mixture was stirred at 60°C for 18 h. The insoluble solid was filtered out and the solution was concentrated. The residue was dissolved in deionized water and extracted with dichloromethane for three times. The combined organic layer was dried with anhydrous Na$_2$SO$_4$, filtered, concentrated, precipitated with diethyl ether and dried in vacuum.

mPEG$_{23}$-N(Boc)$_2$ (2a), white waxy solid, 9.8g, 87.4% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ: 3.85-3.50 (m, 91H), 3.38 (s, 3H), 1.50 (s, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 152.52, 82.12, 71.88, 70.52, 70.15, 69.21, 58.95, 45.15, 28.00.

mPEG$_{45}$-N(Boc)$_2$ (2b), white waxy solid, 9.4g, 88.6% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ: 3.85-3.50 (m, 182H), 3.38 (s, 3H), 1.50 (s, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 152.57, 82.17, 71.92, 70.56, 70.19, 69.26, 59.00, 45.19, 28.04.

mPEG$_{114}$-N(Boc)$_2$ (2c), white solid, 9.5g, 92.7% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ: 3.85-3.50 (m, 455H), 3.38 (s, 3H), 1.50 (s, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 152.51, 82.12, 71.87, 70.51, 70.14, 69.21, 58.96, 45.14, 28.00.

mPEG$_{233}$-N(Boc)$_2$ (2d), white solid, 9.6g, 94.9% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ: 3.85-3.50 (m, 930H), 3.38 (s, 3H), 1.50 (s, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 152.54, 82.16, 71.89, 70.53, 70.17, 69.23, 58.99, 45.16, 28.03.

mPEG$_{485}$-N(Boc)$_2$ (2e), white solid, 9.2g, 91.5% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ: 3.85-3.50 (m, 1939H), 3.38 (s, 3H), 1.50 (s, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 152.65, 82.24, 71.99, 70.62, 69.32, 59.08, 45.25, 28.11.

mPEG$_{682}$-N(Boc)$_2$ (2f), white solid, 9.0g, 90% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ: 3.85-3.55 (m, 2727H), 3.38 (s, 3H), 1.50 (s, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 152.21, 81.77, 71.59, 70.23, 68.93, 58.65, 44.89, 27.73.

mPEG$_{909}$-N(Boc)$_2$ (2g), white solid, 9.0g, 90% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ: 3.85-3.55 (m, 3636H), 3.38 (s, 3H), 1.50 (s, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 152.60, 82.07, 71.70, 70.34, 68.73, 59.10, 45.22, 27.85.
(Boc)$_2$N-PEG$_{227}$-N(Boc)$_2$ (2h), white solid, 10.6g, 85.3% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 3.80-3.50 (m, 91H), 1.50 (s, 36H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 152.73, 82.34, 70.70, 70.33, 69.40, 45.32, 28.18.

(Boc)$_2$N-PEG$_{455}$-N(Boc)$_2$ (2i), white solid, 9.8g, 87.4% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 3.85-3.50 (m, 182H), 1.50 (s, 36H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 152.64, 82.25, 70.62, 70.25, 69.32, 45.25, 28.10.

(Boc)$_2$N-PEG$_{777}$-N(Boc)$_2$ (2j), white solid, 9.7g, 90.7% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 3.85-3.50 (m, 309H), 1.50 (s, 36H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 152.56, 82.17, 70.55, 70.19, 69.25, 45.18, 28.04.

(Boc)$_2$N-PEG$_{150}$-N(Boc)$_2$ (2k), white solid, 9.5g, 91.7% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 3.85-3.50 (m, 600H), 1.50 (s, 36H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 152.52, 82.13, 70.51, 70.15, 69.21, 45.14, 28.01.

(Boc)$_2$N-PEG$_{182}$-N(Boc)$_2$ (2l), white solid, 9.5g, 92.2% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 3.85-3.50 (m, 727H), 1.50 (s, 36H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 152.30, 81.87, 70.31, 69.96, 69.01, 44.96, 27.81.

(Boc)$_2$N-PEG$_{227}$-N(Boc)$_2$ (2m), white solid, 9.5g, 92.8% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 3.85-3.49 (m, 909H), 1.50 (s, 36H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 152.39, 81.98, 70.39, 70.04, 69.09, 45.04, 27.89.

(Boc)$_2$N-PEG$_{455}$-N(Boc)$_2$ (2n), white solid, 9.5g, 93.9% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 3.85-3.50 (m, 1818H), 1.50 (s, 36H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 152.44, 82.03, 72.74, 70.45, 69.15, 45.09, 27.95.

(Boc)$_2$N-PEG$_{795}$-N(Boc)$_2$ (2o), white solid, 9.5g, 94.3% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 3.80-3.55 (m, 3182H), 1.50 (s, 36H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 152.42, 82.02, 70.41, 70.06, 69.11, 45.05, 27.91.

4-ARM-PEG$_{227}$-N(Boc)$_2$ (2p), white solid, 9.3g, 88.7% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 3.85-3.49 (m, 909H), 1.50 (s, 72H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 152.47, 82.06, 70.87, 70.46, 70.10, 69.90, 69.16, 45.10, 27.95.

4-ARM-PEG$_{455}$-N(Boc)$_2$ (2q), white solid, 9.5g, 92.8% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 3.85-3.50 (m, 1818H), 1.50 (s, 72H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 152.58, 82.19, 70.96, 70.56, 70.20, 70.02, 69.26, 45.19, 28.05.
**8-ARM-PEG$_{227}$-N(Boc)$_2$ (2r),** white solid, 9.8g, 89.4% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ: 4.10-3.40 (m, 909H), 1.50 (s, 144H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 152.50, 82.10, 71.34, 70.49, 70.13, 69.72, 69.19, 45.13, 27.99.

**8-ARM-PEG$_{455}$-N(Boc)$_2$ (2s),** white solid, 9.5g, 90.6% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ: 3.85-3.50 (m, 1818H), 1.50 (s, 144H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 152.58, 82.19, 70.56, 70.20, 69.27, 45.19, 28.06.

**8-ARM-PEG$_{795}$-N(Boc)$_2$ (2t),** white solid, 9.6g, 93.7% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ: 3.85-3.50 (m, 3636H), 1.50 (s, 144H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 152.54, 82.14, 71.15, 70.52, 70.15, 69.88, 69.22, 45.15, 28.01.

### 3.3 Typical procedure for the synthesis of PEG-NH$_2$s

To a solution of PEG-N(Boc)$_2$ (2) (0.5 g) in CH$_2$Cl$_2$ (2 mL) at 0℃, TFA (5 mL) dissolved in CH$_2$Cl$_2$ (2 mL) was added dropwise. The solution was stirred under ice bath overnight. The TFA and CH$_2$Cl$_2$ was removed by a rotary evaporator in vacuum. The residue was diluted with deionized water (10 mL) and stirred at 0℃. Ammonium hydroxide (30 mL) was added dropwise until the pH of the solution was 10–11. The solution was stirred for another 15 min and then extracted with CH$_2$Cl$_2$ for three times. The combined organic layer was dried with anhydrous Na$_2$SO$_4$, filtered, concentrated, precipitated with diethyl ether and dried in vacuum.

**mPEG$_{23}$-NH$_2$ (3a),** white solid, 0.33g, 82.5% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ: 3.85-3.50 (m, 89H), 3.38 (s, 3H), 2.87 (t, $J = 4.0$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 73.19, 71.79, 70.43, 70.15, 58.87, 41.63.

**mPEG$_{45}$-NH$_2$ (3b),** white solid, 0.40g, 88.9% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ: 3.80-3.50 (m, 180H), 3.38 (s, 3H), 2.87 (t, $J = 4.0$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 72.96, 71.62, 70.26, 69.97, 58.68, 41.45.

**mPEG$_{114}$-NH$_2$ (3c),** white solid, 0.45g, 93.8% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ: 3.85-3.50 (m, 453H), 3.38 (s, 3H), 2.87 (t, $J = 4.0$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 72.93, 71.90, 70.54, 70.23, 59.00, 41.71.
mPEG$_{233}$-NH$_2$ (3d), white solid, 0.45g, 91.8% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 3.85-3.50 (m, 928H), 3.38 (s, 3H), 2.90 (t, $J = 4.0$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 71.92, 70.55, 59.01, 41.66.

mPEG$_{485}$-NH$_2$ (3e), white solid, 0.46g, 92.9% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 3.85-3.50 (m, 1937H), 3.38 (s, 3H), 3.00 (t, $J = 4.0$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 72.98, 71.41, 70.05, 67.14, 58.46, 40.57.

mPEG$_{682}$-NH$_2$ (3f), white solid, 0.45g, 90.5% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 3.85-3.55 (m, 2725H), 3.38 (s, 3H), 2.88 (t, $J = 5.0$Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 72.92, 71.55, 70.19, 67.27, 58.62, 41.42.

mPEG$_{909}$-NH$_2$ (3g), white solid, 0.45g, 90.4% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 3.85-3.55 (m, 3634H), 3.38 (s, 3H), 2.89 (t, $J = 5.0$Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 72.32, 70.30, 61.32, 42.07.

H$_2$N-PEG$_{23}$-NH$_2$ (3h), white solid, 0.24g, 80.5% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 3.80-3.50 (m, 87H), 2.90 (t, $J = 4.0$ Hz, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 72.44, 70.52, 70.20, 41.50.

H$_2$N-PEG$_{45}$-NH$_2$ (3i), white solid, 0.34g, 85.2% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 3.85-3.49 (m, 178H), 2.87 (t, $J = 4.0$ Hz, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 73.18, 71.20, 70.49, 70.20, 69.85, 41.65.

H$_2$N-PEG$_{77}$-NH$_2$ (3j), white solid, 0.39g, 88.6% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 3.85-3.50 (m, 305H), 2.87(t, $J = 4.0$ Hz, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 73.35, 71.14, 70.51, 70.23, 41.75.

H$_2$N-PEG$_{150}$-NH$_2$ (3k), white solid, 0.43g, 91.5% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 3.85-3.50 (m, 596H), 2.87 (t, $J = 4.0$ Hz, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 73.06, 70.43, 70.13, 41.64.

H$_2$N-PEG$_{182}$-NH$_2$ (3l), white solid, 0.44g, 92.6% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 3.85-3.50 (m, 723H), 2.88 (t, $J = 4.0$ Hz, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 73.12, 70.57, 70.28, 41.76.

H$_2$N-PEG$_{227}$-NH$_2$ (3m), white solid, 0.45g, 93.8% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 3.85-3.49 (m, 905H), 2.87 (t, $J = 4.0$ Hz, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 73.19, 70.52, 70.23, 41.73.

H$_2$N-PEG$_{455}$-NH$_2$ (3n), white solid, 0.45g, 91.8% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 3.85-3.50 (m, 1814H), 2.89 (t, $J = 4.0$ Hz, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 72.45, 70.64, 70.31, 41.68.

H$_2$N-PEG$_{795}$-NH$_2$ (3o), white solid, 0.46g, 92.9% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 3.80-3.55 (m, 3178H), 2.88 (t, $J = 5.0$ Hz, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 71.33, 70.65, 70.38, 41.87.
4-ARM-PEG\textsubscript{227}-NH\textsubscript{2} (3p), white solid, 0.40g, 87% yield. $^1$H NMR (400 MHz, CDCl\textsubscript{3}) $\delta$: 3.85-3.49 (m, 901H), 2.87 (t, $J = 4.0$ Hz, 8H); $^{13}$C NMR (100 MHz, CDCl\textsubscript{3}) $\delta$: 73.36, 70.92, 70.51, 70.29, 70.24, 69.96, 41.76.

4-ARM-PEG\textsubscript{455}-NH\textsubscript{2} (3q), white solid, 0.45g, 93.8% yield. $^1$H NMR (400 MHz, CDCl\textsubscript{3}) $\delta$: 3.85-3.50 (m, 1810H), 2.91 (t, $J = 4.0$ Hz, 8H); $^{13}$C NMR (100 MHz, CDCl\textsubscript{3}) $\delta$: 72.52, 71.08, 70.69, 70.31, 70.17, 41.80.

8-ARM-PEG\textsubscript{227}-NH\textsubscript{2} (3r), white solid, 0.36g, 85.7% yield. $^1$H NMR (400 MHz, CDCl\textsubscript{3}) $\delta$: 3.85-3.50 (m, 893H), 2.87 (t, $J = 4.0$ Hz, 16H); $^{13}$C NMR (100 MHz, CDCl\textsubscript{3}) $\delta$: 73.29, 70.52, 70.24, 69.75, 41.73.

8-ARM-PEG\textsubscript{455}-NH\textsubscript{2} (3s), white solid, 0.41g, 89.1% yield. $^1$H NMR (400 MHz, CDCl\textsubscript{3}) $\delta$: 3.85-3.50 (m, 1802H), 2.87 (t, $J = 4.0$ Hz, 16H); $^{13}$C NMR (100 MHz, CDCl\textsubscript{3}) $\delta$: 73.40, 71.17, 70.54, 70.26, 69.82, 41.79.

8-ARM-PEG\textsubscript{909}-NH\textsubscript{2} (3t), white solid, 0.44g, 91.7% yield. $^1$H NMR (400 MHz, CDCl\textsubscript{3}) $\delta$: 3.85-3.50 (m, 3620H), 2.88 (t, $J = 4.0$ Hz, 16H); $^{13}$C NMR (100 MHz, CDCl\textsubscript{3}) $\delta$: 73.06, 70.57, 70.26, 41.78.

4. Typical procedure for the synthesis of heterodox functional group amino(polyethylene glycol)

4.1 Synthesis of N\textsubscript{3}-PEG\textsubscript{227}-NH\textsubscript{2}

Step 1 Synthesis of Bn-PEG\textsubscript{227}-OAc (4)

Bn-PEG\textsubscript{227}-OH (50g, 1.0 eq) was dissolved with anhydrous dichloromethane (450 mL) in a round-bottomed flask follow by the addition of triethylamine (3 eq). The solution was then stirred at 0°C for 15min. Acetic anhydride (2 eq) was dissolved in anhydrous dichloromethane (50 mL) and added dropwise to the solution. The resulting mixture was stirred at room temperature overnight. The solution was quenched by water, and extracted with dichloromethane for three times. The combined organic layer was dried with anhydrous Na\textsubscript{2}SO\textsubscript{4}, filtered, concentrated, precipitated with diethyl ether and dried under vacuum, to give Bn-PEG\textsubscript{227}-OAc as a white solid, 51.6g, 99% yield. $^1$H NMR (400 MHz, CDCl\textsubscript{3}) $\delta$: 7.38-7.24 (m, 5H), 4.57 (s, 2H), 4.22 (t, $J = 4.0$ Hz, 2H), 3.85-3.50 (m, 89H), 2.08 (s, 3H); $^{13}$C NMR (100 MHz, CDCl\textsubscript{3}) $\delta$: 170.90, 138.25, 128.29, 127.65, 127.51, 73.15, 70.53, 69.40, 69.06, 63.54, 20.91.
Step 2 Synthesis of AcO-PEG$_{27}$-OH (5)
BnO-PEG$_{27}$-OAc (4) (48g, 1.0 eq) was dissolved in CH$_3$OH (200 mL), then 10% Pd/C (0.03%) was added carefully. The solution was vacuumed for argon and then hydrogen was introduced slowly. The resulting mixture was stirred overnight at 40°C with the protection of hydrogen. After the reaction was completed, Pd/C was filtered and CH$_3$OH was removed. The residue was precipitated with diethyl ether and dried under vacuum, to give AcO-PEG$_{27}$-OH as a white solid, 40.4g, 99% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ: 4.22 (t, $J$ = 4.0 Hz, 2H), 3.85-3.50 (m, 89H), 2.08 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 170.95, 72.50, 70.53, 70.32, 69.07, 63.55, 61.64, 20.91.

Step 3 Synthesis of AcO-PEG$_{27}$-OMs (6)
AcO-PEG$_{27}$-OH (5) (40g, 1.0 eq) was dissolved with anhydrous dichloromethane (350 mL) in a round-bottomed flask followed by the addition of triethylamine (2 eq). The solution was then stirred at 0°C for 15min. MsCl (1.2 eq) was dissolved in anhydrous dichloromethane (50 mL) and added dropwise to the solution. The resulting mixture was stirred at room temperature overnight. The solution was quenched by water, and extracted with dichloromethane for three times. The combined organic layer was dried with anhydrous Na$_2$SO$_4$, filtered, concentrated, precipitated with diethyl ether and dried under vacuum, to give AcO-PEG$_{27}$-OMs as a yellow solid, 42.7g, 99% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ: 4.38 (t, $J$ = 4.0Hz, 2H), 4.22 (t, $J$ = 4.0 Hz, 2H), 3.85-3.50 (m, 87H), 3.09 (s, 3H), 2.08 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 170.89, 70.51, 69.29, 69.05, 68.96, 63.52, 37.66, 20.90.

Step 4 Synthesis of AcO-PEG$_{27}$-N$_3$ (7)
To a solution of AcO-PEG$_{27}$-OMs (6) (35g, 1.0 eq) dissolved in anhydrous C$_2$H$_5$OH (350 mL), NaN$_3$ (1.5 eq) was added. The resulting mixture was refluxed overnight at 80°C for 18h. The solution was quenched by water, and C$_2$H$_5$OH was removed in vacuum. The residue was dissolved in water and extracted with CH$_2$Cl$_2$ for three times. The combined organic layer was dried with anhydrous Na$_2$SO$_4$, filtered, concentrated, precipitated with diethyl ether and dried under vacuum, to give AcO-PEG$_{27}$-N$_3$ as a white solid, 32.8g, 99% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ: 4.22 (t, $J$ = 4.0 Hz, 2H), 3.85-3.50 (m, 87H), 3.39 (t, $J$ = 4.0 Hz, 2H), 2.08 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 170.88, 70.51, 69.97, 69.04, 68.96, 63.52, 50.60, 20.89.

Step 5 Synthesis of N$_3$-PEG$_{27}$-OH (8)
To a solution of AcO-PEG$_{27}$-N$_3$ (7) (30g, 1.0 eq) dissolved in water (300 mL), NaOH (2.0 eq) was
added. Then the solution was stirred at room temperature for 18 h. The solution was extracted with CH$_2$Cl$_2$ for three times. The combined organic layer was dried with anhydrous Na$_2$SO$_4$, filtered, concentrated, precipitated with diethyl ether and dried under vacuum, to give N$_3$-PEG$_{27}$-OH as a white solid, 28.4g, 99% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 3.85-3.50 (m, 89H), 3.39 (t, $J = 4.0$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 72.41, 70.41, 70.20, 69.88, 61.46, 50.51.

**Step 6 Synthesis of N$_3$-PEG$_{27}$-OMs (9)**

N$_3$-PEG$_{27}$-OH (8) (25g, 1.0 eq) was dissolved with anhydrous dichloromethane (250 mL) in a round-bottomed flask followed by the addition of triethylamine (2 eq). The solution was then stirred at 0°C for 15min. MsCl (1.2 eq) was dissolved in anhydrous dichloromethane (50 mL) and added dropwise to the solution. The resulting mixture was stirred at room temperature overnight. The solution was quenched by water, and extracted with dichloromethane for three times. The combined organic layer was dried with anhydrous Na$_2$SO$_4$, filtered, concentrated, precipitated with diethyl ether and dried under vacuum, to give N$_3$-PEG$_{27}$-OMs as a white solid, 26.7g, 99% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 4.38 (t, $J = 4.0$Hz, 2H), 3.85-3.50 (m, 87H), 3.39 (t, $J = 4.0$ Hz, 2H), 3.08 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 71.88, 70.52, 69.98, 58.96, 50.62.

**Step 7 Synthesis of N$_3$-PEG$_{27}$-N(Boc)$_2$ (10)**

N$_3$-PEG$_{27}$-OMs (9) (1) (20g, 1.0 eq) was dissolved with anhydrous acetonitrile (200 mL) in a round-bottomed flask. Then, t-BuOK (3.0 eq) and (Boc)$_2$NH (3.0 eq) were added to the solution. The mixture was stirred at 60°C for 18 h. The insoluble solid was filtered out and the solution was concentrated. The residue was dissolved in deionized water and extracted with dichloromethane for three times. The combined organic layer was dried with anhydrous Na$_2$SO$_4$, filtered, concentrated, precipitated with diethyl ether and dried under vacuum, to give N$_3$-PEG$_{27}$-N(Boc)$_2$ as a white solid, 22.2g, 99% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 3.85-3.50 (m, 89H), 3.39 (t, $J = 4.0$ Hz, 2H), 1.50 (s, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 152.54, 82.14, 70.53, 70.16, 69.99, 69.22, 53.51, 50.63, 45.16, 28.01.

**Step 8 Synthesis of N$_3$-PEG$_{27}$-NH$_2$**

To a solution of N$_3$-PEG$_{27}$-N(Boc)$_2$ (10) (0.5 g) in CH$_2$Cl$_2$ (2 mL) at 0°C, TFA (5 mL) dissolved in CH$_2$Cl$_2$ (2 mL) was added dropwise. The solution was stirred under ice bath overnight. The TFA and CH$_2$Cl$_2$ was removed by a rotary evaporator in vacuum. The residue was diluted with deionized water (10 mL) and stirred at 0°C. Ammonium hydroxide (30 mL) was added dropwise until the pH
of the solution was 10~11. The solution was stirred for another 15 min and then extracted with CH$_2$Cl$_2$ for three times. The combined organic layer was dried with anhydrous Na$_2$SO$_4$, filtered, concentrated, precipitated with diethyl ether and dried under vacuum, to give N$_3$-PEG$_{23}$-NH$_2$ as a white solid, 0.396g, 99% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 3.85-3.50 (m, 87H), 3.39 (t, $J = 4.0$Hz, 2H), 2.89 (t, $J = 4.0$Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 72.63, 70.52, 70.19, 69.99, 50.63, 41.60.

4.2 Synthesis of Alkyne-PEG$_{27}$-NH$_2$

Step 1 Synthesis of Bn-PEG$_{27}$-Alkyne (11)

To a solution of Bn-PEG$_{27}$-OH (50g, 1.0 eq) dissolved in anhydrous THF (400 mL), NaH (3.0 eq) was added in batches at 0$^\circ$C. After stirring for more than 30 min, 3-bromopropyl (3.0 eq) dissolved in THF (50 mL) was added dropwise. The resulting mixture was stirred at room temperature for 18 h under the protection of argon. The excess NaH was quenched by adding deionized water dropwise and the solvent was removed in vacuum. The residue was dissolved in deionized water and extracted with CH$_2$Cl$_2$ three times. The combined organic layer was dried with anhydrous Na$_2$SO$_4$, filtered, concentrated, precipitated with diethyl ether and dried under vacuum, to give Bn-PEG$_{27}$-Alkyne as a yellow solid, 51.4g, 99% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.39 -7 .22 (m, 5H), 4.56 (s, 2H), 4.20 (s, 2H), 3.85-3.50 (m, 91H), 2.46 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 137.94, 127.93, 127.26, 127.14, 79.31, 74.56, 72.74, 70.17, 69.99, 69.08, 68.66, 57.95.

Step 2 Synthesis of Alkyne-PEG$_{27}$-OH (12)

Bn-PEG$_{27}$-Alkyne (11) (48g) was added to a round-bottomed flask followed by the addition of TFA (250 mL). The solution was stirred at 90$^\circ$C by reflux for 18 h. TFA was removed. The residue was dissolved in deionized water and extracted with CH$_2$Cl$_2$ three times. The combined organic layer was dried with anhydrous Na$_2$SO$_4$, filtered, concentrated, precipitated with diethyl ether and dried under vacuum. The product was dissolved in 1, 4-dioxane (300 mL) followed by the addition of activated carbon (45 g). The mixture was stirred at 40$^\circ$C for 12 h. Activated carbon was filtered off. The solvent was removed and the residue was precipitated with diethyl ether and dried under vacuum, to give Alkyne-PEG$_{27}$-OH as a white solid, 40.4g, 99% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 4.20 (d, $J = 4.0$ Hz, 2H), 3.85-3.50 (m, 91H), 2.45 (t, $J =4.0$Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 79.52, 74.61, 72.41, 70.40, 70.22, 68.91, 61.45, 58.20.
Step 3 Synthesis of Alkyne-PEG$_{27}$-OMs (13)

Alkyne-PEG$_{27}$-OH (12) (40g, 1.0 eq) was dissolved with anhydrous dichloromethane (400 mL) in a round-bottomed flask followed by the addition of triethylamine (2 eq). The solution was then stirred at 0°C for 15min. MsCl (1.2 eq) was dissolved in anhydrous dichloromethane (50 mL) and added dropwise to the solution. The resulting mixture was stirred at room temperature overnight. The solution was quenched by water, and extracted with dichloromethane for three times. The combined organic layer was dried with anhydrous Na$_2$SO$_4$, filtered, concentrated, precipitated with diethyl ether and dried under vacuum, to give Alkyne-PEG$_{27}$-OMs as a yellow solid, 42.7g, 99% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ: 4.38 (t, $J = 4.0$ Hz, 2H), 4.20 (d, $J = 4.0$ Hz, 2H), 3.85-3.50 (m, 100H), 3.08 (s, 3H), 2.44 (t, $J = 4.0$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 79.64, 74.63, 70.51, 70.35, 69.29, 69.04, 68.96, 58.33, 37.67.

Step 4 Synthesis of Alkyne-PEG$_{27}$-N(Boc)$_2$ (14)

Alkyne-PEG$_{27}$-OMs (13) (1) (35g, 1.0 eq) was dissolved with anhydrous acetonitrile (350 mL) in a round-bottomed flask. Then, t-BuOK (3.0 eq) and (Boc)$_2$NH (3.0 eq) were added to the solution. The mixture was stirred at 60°C for 18 h. The insoluble solid was filtered out and the solution was concentrated. The residue was dissolved in deionized water and extracted with dichloromethane for three times. The combined organic layer was dried with anhydrous Na$_2$SO$_4$, filtered, concentrated, precipitated with diethyl ether and dried under vacuum, to give Alkyne-PEG$_{27}$-N(Boc)$_2$ as a yellow solid, 38.8g, 99% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ: 4.20 (d, $J = 4.0$ Hz, 2H), 3.85-3.50 (m, 102H), 2.44 (t, $J = 4.0$ Hz, 1H), 1.50 (s, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 152.64, 82.26, 79.71, 74.66, 70.62, 70.25, 69.32, 69.15, 58.44, 45.24, 28.10.

Step 5 Synthesis of Alkyne-PEG$_{27}$-NH$_2$

To a solution of Alkyne-PEG$_{27}$-N(Boc)$_2$ (14) (0.5 g) in CH$_2$Cl$_2$ (2 mL) at 0°C, TFA (5 mL) dissolved in CH$_2$Cl$_2$ (2 mL) was added dropwise. The solution was stirred under ice bath overnight. The TFA and CH$_2$Cl$_2$ was removed by a rotary evaporator in vacuum. The residue was diluted with deionized water (10 mL) and stirred at 0°C. Ammonium hydroxide (30 mL) was added dropwise until the pH of the solution was 10~11. The solution was stirred for another 15 min and then extracted with CH$_2$Cl$_2$ for three times. The combined organic layer was dried with anhydrous Na$_2$SO$_4$, filtered, concentrated, precipitated with diethyl ether and dried under vacuum, to give Alkyne-PEG$_{27}$-NH$_2$ as a yellow solid, 0.396g, 99% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ: 4.20 (d, $J = 4.0$ Hz, 2H), 3.85-
3.50 (m, 100H), 2.87 (t, $J = 4.0$ Hz, 2H), 2.44 (t, $J = 4.0$ Hz, 1H); $^{13}$C NMR (100MHz, CDCl$_3$) δ: 79.61, 74.63, 73.13, 70.50, 70.33, 70.20, 69.02, 58.31, 41.71.

5. Synthesis of mPEG$_{114}$-GSH

5.1 Synthesis of mPEG$_{114}$-Mal

To a solution of Mal-COOH (1.0 eq) dissolved in CH$_2$Cl$_2$(10 mL), HOBt (2.0 eq) and EDCI (2.0 eq) was added. The mixture was stirred at room temperature for 2 h. Then mPEG$_{114}$-NH$_2$(1g, 1.0 eq) was added and the resulting mixture was reacted at room temperature for 48 h. The blocker 1, 4-p-diphenol was added and the solvent was removed. After that, the residue was dissolved in deionized water (50 mL) followed by the addition of HCl (10 mL, 1 mol/L). The solution was stirred for 2 h, and the insoluble matter was filtered off. The solution was extracted with CH$_2$Cl$_2$ for three times. The combined organic layer was dried with anhydrous Na$_2$SO$_4$, filtered, concentrated, precipitated with diethyl ether and dried under vacuum, to give mPEG$_{114}$-Mal as a white solid, 0.98g, 95% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ: 6.70 (s, 2H), 3.85-3.50 (m, 453H), 3.38 (s, 3H), 2.52 (t, $J = 4.0$ Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ:175.92, 175.02, 137.05, 60.03, 41.50, 37.18, 37.01.

5.2 Synthesis of mPEG$_{114}$-GSH

To a solution of mPEG$_{114}$-Mal (0.5g, 1.0 eq) dissolved in acetonitrile and deionized water, GSH (3.0 eq), TFA (3.0 eq), PBS (100 µL) were added. The solution was stirred at 30°C for 48 h. The solvent was removed. The residue was dissolved in deionized water and extracted with CH$_2$Cl$_2$ for three times. The combined organic layer was dried with anhydrous Na$_2$SO$_4$, filtered, concentrated, precipitated with diethyl ether and dried under vacuum, to give mPEG$_{114}$-GSH as a white solid, 0.525g, 99% yield. $^{13}$C NMR (100 MHz, D$_2$O) δ:181.31, 180.09, 177.40, 177.01, 176.28, 175.64, 174.41, 60.53, 56.56, 55.28, 44.83, 41.56, 38.32, 36.07, 33.89, 28.65.
6. Supplemental Schemes, Tables, and Figures

Scheme S1. Chemical structure of mPEG$\textsubscript{n}$-OMss, MsO-PEG$\textsubscript{n}$-OMss, 4-arm-PEG$\textsubscript{n}$-OMss and 8-arm-PEG$\textsubscript{n}$-OMss

Scheme S2. Chemical structure of mPEG$\textsubscript{n}$-N(Boc)$_2$S, (Boc)$_2$N-PEG$\textsubscript{n}$-N(Boc)$_2$S, 4-arm-PEG$\textsubscript{n}$-N(Boc)$_2$S and 8-arm-PEG$\textsubscript{n}$-N(Boc)$_2$S
**Scheme S3** The synthetic route of N$_3$-PEG$_{27}$-NH$_2$

**Scheme S4** The synthetic route of Alk-PEG$_{27}$-NH$_2$
**Table S1** Optimization of reaction conditions for the synthesis of mPEG$_{23}$-N(Boc)$_2$\textsuperscript{a}

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<th>Entry</th>
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<th>Solvent</th>
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<th>Temp (℃)</th>
<th>Yield (%)\textsuperscript{b}</th>
<th>End-group fidelity (\textsuperscript{1}H NMR)\textsuperscript{c}</th>
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\textsuperscript{a}Reaction conditions: mPEG$_{23}$-OMs (1) (1.0 eq) were added to a mixture of (Boc)$_2$NH/base (1:1) in 10.0 mL of anhydrous solvent, and stirred for 18 h. \textsuperscript{b}Isolated yield. \textsuperscript{c}End-group fidelity of 2 were determined by \textsuperscript{1}H NMR.
**Fig. S1** $^1$H NMR of mPEG$_{23}$-OMs (1a) (400 MHz, CDCl$_3$)

**Fig. S2** $^{13}$C NMR of mPEG$_{23}$-OMs (1a) (100 MHz, CDCl$_3$)
**Fig. S3** SEC of mPEG<sub>23</sub>-OMs (1a) (DMF, 1.00 mL/min, PS as standard)

**Fig. S4** <sup>1</sup>H NMR of mPEG<sub>45</sub>-OMs (1b) (400 MHz, CDCl<sub>3</sub>)
**Fig. S5** $^{13}$C NMR of mPEG$_{45}$-OMs (1b) (100 MHz, CDCl$_3$)

**Fig. S6** SEC of mPEG$_{45}$-OMs (1b) (DMF, 1.00 mL/min, PS as standard)
Fig. S7 $^1$H NMR of mPEG$_{114}$-OMs (1c) (400 MHz, CDCl$_3$)

Fig. S8 $^{13}$C NMR of mPEG$_{114}$-OMs (1c) (100 MHz, CDCl$_3$)
Fig. S9 $^1$H NMR of mPEG$_{233}$-OMs (1d) (400 MHz, CDCl$_3$)

Fig. S10 $^{13}$C NMR of mPEG$_{233}$-OMs (1d) (100 MHz, CDCl$_3$)
Fig. S11 $^1$H NMR of mPEG$_{485}$-OMs (1e) (400 MHz, CDCl$_3$)

Fig. S12 $^{13}$C NMR of mPEG$_{485}$-OMs (1e) (100 MHz, CDCl$_3$)
Fig. S13 $^1$H NMR of mPEG$_{682}$-OMs (1f) (400 MHz, CDCl$_3$)

Fig. S14 $^{13}$C NMR of mPEG$_{682}$-OMs (1f) (100 MHz, CDCl$_3$)
**Fig. S15** $^1$H NMR of mPEG$_{909}$-OMs (1g) (400 MHz, CDCl$_3$)

**Fig. S16** $^{13}$C NMR of mPEG$_{909}$-OMs (1g) (100 MHz, CDCl$_3$)
**Fig. S17** $^1$H NMR of MsO-PEG$_{23}$-OMs (1h) (400 MHz, CDCl$_3$)

**Fig. S18** $^{13}$C NMR of MsO-PEG$_{23}$-OMs (1h) (100 MHz, CDCl$_3$)
**Fig. S19** $^1$H NMR of MsO-PEG$_{45}$-OMs (Ii) (400 MHz, CDCl$_3$)

**Fig. S20** $^{13}$C NMR of MsO-PEG$_{45}$-OMs (Ii) (100 MHz, CDCl$_3$)
**Fig. S21** $^1$H NMR of MsO-PEG$_{77}$-OMs (1j) (400 MHz, CDCl$_3$)

**Fig. S22** $^{13}$C NMR of MsO-PEG$_{77}$-OMs (1j) (100 MHz, CDCl$_3$)
Fig. S23 $^1$H NMR of MsO-PEG$_{150}$-OMs (1k) (400 MHz, CDCl$_3$)

Fig. S24 $^{13}$C NMR of MsO-PEG$_{150}$-OMs (1k) (100 MHz, CDCl$_3$)
Fig. S25 $^1$H NMR of MsO-PEG$_{182}$-OMs (1I) (400 MHz, CDCl$_3$)

Fig. S26 $^{13}$C NMR of MsO-PEG$_{182}$-OMs (1I) (100 MHz, CDCl$_3$)
Fig. S27 ¹H NMR of MsO-PEG₂₂₇-OMs (1m) (400 MHz, CDCl₃)

Fig. S28 ¹³C NMR of MsO-PEG₂₂₇-OMs (1m) (100 MHz, CDCl₃)
Fig. S29 $^1$H NMR of MsO-PEG$_{455}$-OMs (1n) (400 MHz, CDCl$_3$)

Fig. S30 $^{13}$C NMR of MsO-PEG$_{455}$-OMs (1n) (100 MHz, CDCl$_3$)
**Fig. S31** $^1$H NMR of MsO-PEG$_{795}$-OMs (1o) (400 MHz, CDCl$_3$)

**Fig. S32** $^{13}$C NMR of MsO-PEG$_{795}$-OMs (1o) (100 MHz, CDCl$_3$)
Fig. S33 $^1$H NMR of 4-ARM-PEG$_{227}$-OMs (1p) (400 MHz, CDCl$_3$)

Fig. S34 $^{13}$C NMR of 4-ARM-PEG$_{227}$-OMs (1p) (100 MHz, CDCl$_3$)
Fig. S35 $^1$H NMR of 4-ARM-PEG$_{455}$-OMs (1q) (400 MHz, CDCl$_3$)

Fig. S36 $^{13}$C NMR of 4-ARM-PEG$_{455}$-OMs (1q) (100 MHz, CDCl$_3$)
Fig. S37 $^1$H NMR of 8-ARM-PEG$_{227}$-OMs (1r) (400 MHz, CDCl$_3$)

Fig. S38 $^{13}$C NMR of 8-ARM-PEG$_{227}$-OMs (1r) (100 MHz, CDCl$_3$)
**Fig. S39** $^1$H NMR of 8-ARM-PEG$_{455}$-OMs (1s) (400 MHz, CDCl$_3$)

**Fig. S40** $^{13}$C NMR of 8-ARM-PEG$_{455}$-OMs (1s) (100 MHz, CDCl$_3$)
Fig. S41 $^1$H NMR of 8-ARM-PEG$_{300}$-OMs (1t) (400 MHz, CDCl$_3$)

Fig. S42 $^{13}$C NMR of 8-ARM-PEG$_{300}$-OMs (1t) (100 MHz, CDCl$_3$)
Fig. S43 $^1$H NMR of mPEG$_{23}$-N(Boc)$_2$ (2a) (400 MHz, CDCl$_3$)

Fig. S44 $^1$H NMR of mPEG$_{45}$-N(Boc)$_2$ (2b) (400 MHz, CDCl$_3$)
Fig. S45 $^{13}$C NMR of mPEG$_{45}$-N(Boc)$_2$ (2b) (100MHz, CDCl$_3$)

Fig. S46 SEC of mPEG$_{45}$-N(Boc)$_2$ (2b) (DMF, 1.00 mL/min, PS as standard)
Fig. S47 $^1$H NMR of mPEG$_{114}$-N(Boc)$_2$ (2c) (400 MHz, CDCl$_3$)

Fig. S48 $^{13}$C NMR of mPEG$_{114}$-N(Boc)$_2$ (2c) (100 MHz, CDCl$_3$)
Fig. S49 $^1$H NMR of mPEG$_{233}$-N(Boc)$_2$ (2d) (400 MHz, CDCl$_3$)

Fig. S50 $^{13}$C NMR of mPEG$_{233}$-N(Boc)$_2$ (2d) (100 MHz, CDCl$_3$)
Fig. S51 $^1$H NMR of mPEG$_{485}$-N(Boc)$_2$ (2e) (400 MHz, CDCl$_3$)

Fig. S52 $^{13}$C NMR of mPEG$_{485}$-N(Boc)$_2$ (2e) (100 MHz, CDCl$_3$)
Fig. S53 $^1$H NMR of mPEG$_{682}$-N(Boc)$_2$ (2f) (400 MHz, CDCl$_3$)

Fig. S54 $^{13}$C NMR of mPEG$_{682}$-N(Boc)$_2$ (2f) (100 MHz, CDCl$_3$)
**Fig. S55** $^1$H NMR of mPEG$_{909}$-N(Boc)$_2$ (2g) (400 MHz, CDCl$_3$)

**Fig. S56** $^{13}$C NMR of mPEG$_{909}$-N(Boc)$_2$ (2g) (100 MHz, CDCl$_3$)
**Fig. S57** $^1$H NMR of (Boc)$_2$N-PEG$_{23}$-N(Boc)$_2$ (2h) (400 MHz, CDCl$_3$)

**Fig. S58** $^{13}$C NMR of (Boc)$_2$N-PEG$_{23}$-N(Boc)$_2$ (2h) (100 MHz, CDCl$_3$)
Fig. S59 ¹H NMR of (Boc)₂N-PEG₄₅-N(Boc)₂ (2i) (400 MHz, CDCl₃)

Fig. S60 ¹³C NMR of (Boc)₂N-PEG₄₅-N(Boc)₂ (2i) (100 MHz, CDCl₃)
Fig. S61 $^1$H NMR of (Boc)$_2$N-PEG$_{77}$-N(Boc)$_2$ (2j) (400 MHz, CDCl$_3$)

Fig. S62 $^{13}$C NMR of (Boc)$_2$N-PEG$_{77}$-N(Boc)$_2$ (2j) (100 MHz, CDCl$_3$)
**Fig. S63** $^1$H NMR of (Boc)$_2$N-PEG$_{150}$-N(Boc)$_2$ (2k) (400 MHz, CDCl$_3$)

**Fig. S64** $^{13}$C NMR of (Boc)$_2$N-PEG$_{150}$-N(Boc)$_2$ (2k) (100 MHz, CDCl$_3$)
**Fig. S65** $^1$H NMR of $(\text{Boc})_2\text{N-PEG}_{182}\text{-N(Boc)}_2$ (2I) (400 MHz, CDCl$_3$)

**Fig. S66** $^{13}$C NMR of $(\text{Boc})_2\text{N-PEG}_{182}\text{-N(Boc)}_2$ (2I) (100 MHz, CDCl$_3$)
Fig. S67 $^1$H NMR of (Boc)$_2$N-PEG$_{227}$-N(Boc)$_2$ (2m) (400MHz, CDCl$_3$)

Fig. S68 $^{13}$C NMR of (Boc)$_2$N-PEG$_{227}$-N(Boc)$_2$ (2m) (100MHz, CDCl$_3$)
Fig. S69 $^1$H NMR of (Boc)$_2$N-PEG$_{455}$-N(Boc)$_2$ (2n) (400 MHz, CDCl$_3$)

Fig. S70 $^{13}$C NMR of (Boc)$_2$N-PEG$_{455}$-N(Boc)$_2$ (2n) (100 MHz, CDCl$_3$)
Fig. S71 $^1$H NMR of (Boc)$_2$N-PEG$_{795}$-N(Boc)$_2$ (2o) (400 MHz, CDCl$_3$)

Fig. S72 $^{13}$C NMR of (Boc)$_2$N-PEG$_{795}$-N(Boc)$_2$ (2o) (100 MHz, CDCl$_3$)
Fig. S73 $^1$H NMR of 4-ARM-PEG$_{227}$-N(Boc)$_2$ (2p) (400 MHz, CDCl$_3$)

Fig. S74 $^{13}$C NMR of 4-ARM-PEG$_{227}$-N(Boc)$_2$ (2p) (100 MHz, CDCl$_3$)
**Fig. S75** $^1$H NMR of 4-ARM-PEG$_{455}$-N(Boc)$_2$ (2q) (400 MHz, CDCl$_3$)

**Fig. S76** $^{13}$C NMR of 4-ARM-PEG$_{455}$-N(Boc)$_2$ (2q) (100 MHz, CDCl$_3$)
"Fig. S77 $^1$H NMR of 8-ARM-PEG$_{227}$-N(Boc)$_2$ (2r) (400 MHz, CDCl$_3$)"

"Fig. S78 $^{13}$C NMR of 8-ARM-PEG$_{227}$-N(Boc)$_2$ (2r) (100 MHz, CDCl$_3$)"
Fig. S79 $^1$H NMR of 8-ARM-PEG$_{455}$-N(Boc)$_2$ (2s) (400 MHz, CDCl$_3$)

Fig. S80 $^{13}$C NMR of 8-ARM-PEG$_{455}$-N(Boc)$_2$ (2s) (100 MHz, CDCl$_3$)
**Fig. S81** $^1$H NMR of 8-ARM-PEG$_{800}$-N(Boc)$_2$ (2t) (400 MHz, CDCl$_3$)

**Fig. S82** $^{13}$C NMR of 8-ARM-PEG$_{800}$-N(Boc)$_2$ (2t) (100 MHz, CDCl$_3$)
Fig. S83 $^1$H NMR of mPEG$_{23}$-NH$_2$ (3a) (400 MHz, CDCl$_3$)

Fig. S84 $^1$H NMR of mPEG$_{45}$-NH$_2$ (3b) (400 MHz, CDCl$_3$)
**Fig. S85** $^{13}$C NMR of mPEG$_{45}$-NH$_2$ (3b) (100 MHz, CDCl$_3$)

**Fig. S86** SEC of mPEG$_{45}$-NH$_2$ (3b) (DMF, 1.00 mL/min, PS as standard)
Fig. S87 $^1$H NMR of mPEG$_{114}$-NH$_2$ (3c) (400 MHz, CDCl$_3$)

Fig. S88 $^{13}$C NMR of mPEG$_{114}$-NH$_2$ (3c) (100 MHz, CDCl$_3$)
**Fig. S89** $^1$H NMR of mPEG$_{233}$-NH$_2$(3d) (400 MHz, CDCl$_3$)

**Fig. S90** $^{13}$C NMR of mPEG$_{233}$-NH$_2$(3d) (100 MHz, CDCl$_3$)
Fig. S91 SEC of mPEG$_{233}$-NH$_2$ (3d) (DMF, 1.00 mL/min, PS as standard)

Fig. S92 $^1$H NMR of mPEG$_{485}$-NH$_2$ (3e) (400 MHz, CDCl$_3$)
Fig. S93 $^{13}$C NMR of mPEG$_{485}$-NH$_2$ (3e) (100 MHz, CDCl$_3$)

Fig. S94 SEC of mPEG$_{485}$-NH$_2$ (3e) (DMF, 1.00 mL/min, PS as standard)
Fig. S95 \(^1\)H NMR of mPEG\(_{682}\)-NH\(_2\) (3f) (400 MHz, CDCl\(_3\))

Fig. S96 \(^{13}\)C NMR of mPEG\(_{682}\)-NH\(_2\) (3f) (100 MHz, CDCl\(_3\))
**Fig. S97** SEC of mPEG$_{682}$-NH$_2$ (3f) (DMF, 1.00 mL/min, PS as standard)

**Fig. S98** $^1$H NMR of mPEG$_{909}$-NH$_2$ (3g) (400 MHz, CDCl$_3$)
**Fig. S99** $^{13}$C NMR of mPEG$_{909}$-NH$_2$ (3g) (100 MHz, CDCl$_3$)

**Fig. S100** SEC of mPEG$_{909}$-NH$_2$ (3g) (DMF, 1.00 mL/min, PS as standard)
Fig. S101 $^1$H NMR of H$_2$N-PEG$_{23}$-NH$_2$ (3h) (400 MHz, CDCl$_3$)

Fig. S102 $^{13}$C NMR of H$_2$N-PEG$_{23}$-NH$_2$ (3h) (100 MHz, CDCl$_3$)
Fig. S103 ¹H NMR of H₂N-PEG₄₅-NH₂ (3I) (400 MHz, CDCl₃)

Fig. S104 ¹³C NMR of H₂N-PEG₄₅-NH₂ (3I) (100 MHz, CDCl₃)
**Fig. S105** $^1$H NMR of H$_2$N-PEG$_{77}$-NH$_2$ (3j) (400 MHz, CDCl$_3$)

**Fig. S106** $^{13}$C NMR of H$_2$N-PEG$_{77}$-NH$_2$ (3j) (100 MHz, CDCl$_3$)
Fig. S107: $^1$H NMR of $\text{H}_2\text{N-PEG}_{150}-\text{NH}_2$ (3k) (400 MHz, CDCl$_3$)

Fig. S108: $^{13}$C NMR of $\text{H}_2\text{N-PEG}_{150}-\text{NH}_2$ (3k) (100 MHz, CDCl$_3$)
**Fig. S109** $^1$H NMR of H$_2$N-PEG$_{182}$-NH$_2$ (3l) (400 MHz, CDCl$_3$)

**Fig. S110** $^{13}$C NMR of H$_2$N-PEG$_{182}$-NH$_2$ (3l) (100 MHz, CDCl$_3$)
**Fig. S111** ¹H NMR of H₃N-PEG₂₂₇-NH₂ (3m) (400 MHz, CDCl₃)

**Fig. S112** ¹³C NMR of H₃N-PEG₂₂₇-NH₂ (3m) (100 MHz, CDCl₃)
**Fig. S113** SEC of H$_2$N-PEG$_{227}$-NH$_2$ (3m) (DMF, 1.00 mL/min, PS as standard)

**Fig. S114** $^1$H NMR of H$_2$N-PEG$_{455}$-NH$_2$ (3n) (400 MHz, CDCl$_3$)
Fig. S115 $^{13}$C NMR of H$_2$N-PEG$_{455}$-NH$_2$ (3n) (100 MHz, CDCl$_3$)

Fig. S116 $^1$H NMR of H$_2$N-PEG$_{795}$-NH$_2$ (3o) (400 MHz, CDCl$_3$)
**Fig. S117** $^{13}$C NMR of H$_2$N-PEG$_{795}$-NH$_2$ (3o) (100 MHz, CDCl$_3$)

**Fig. S118** $^1$H NMR of 4-ARM-PEG$_{227}$-NH$_2$ (3p) (400 MHz, CDCl$_3$)
**Fig. S119** $^{13}$C NMR of 4-ARM-PEG$_{227}$-NH$_2$ (3p) (100 MHz, CDCl$_3$)

**Fig. S120** SEC of 4-ARM-PEG$_{227}$-NH$_2$ (3p) (DMF, 1.00 mL/min, PS as standard)
**Fig. S121** $^1$H NMR of 4-ARM-PEG$_{455}$-NH$_2$ (3q) (400 MHz, CDCl$_3$)

**Fig. S122** $^{13}$C NMR of 4-ARM-PEG$_{455}$-NH$_2$ (3q) (100 MHz, CDCl$_3$)
**Fig. S123** $^1$H NMR of 8-ARM-PEG$_{227}$-NH$_2$ (3r) (400 MHz, CDCl$_3$)

**Fig. S124** $^{13}$C NMR of 8-ARM-PEG$_{227}$-NH$_2$ (3r) (100 MHz, CDCl$_3$)
Fig. S125 $^1$H NMR of 8-ARM-PEG$_{455}$-NH$_2$ (3s) (400 MHz, CDCl$_3$)

Fig. S126 $^{13}$C NMR of 8-ARM-PEG$_{455}$-NH$_2$ (3s) (100 MHz, CDCl$_3$)
Fig. S127 $^1$H NMR of 8-ARM-PEG$_{909}$-NH$_2$ (3t) (400 MHz, CDCl$_3$)

Fig. S128 $^{13}$C NMR of 8-ARM-PEG$_{909}$-NH$_2$ (3t) (100 MHz, CDCl$_3$)
Fig. S129 $^1$H NMR of Bn-PEG$_{27}$-OAc (4) (400 MHz, CDCl$_3$)

Fig. S130 $^{13}$C NMR of Bn-PEG$_{27}$- OAc (4) (100 MHz, CDCl$_3$)
Fig. S131 $^1$H NMR of AcO-PEG$_{27}$-OH (5) (400 MHz, CDCl$_3$)

Fig. S132 $^{13}$C NMR of AcO-PEG$_{27}$-OH (5) (100 MHz, CDCl$_3$)
**Fig. S133** $^1$H NMR of AcO-PEG$_{27}$-OMs (6) (400 MHz, CDCl$_3$)

**Fig. S134** $^{13}$C NMR of AcO-PEG$_{27}$-OMs (6) (100 MHz, CDCl$_3$)
Fig. S135 ¹H NMR of AcO-PEG₂₇₋₃₇ (7) (400 MHz, CDCl₃)

Fig. S136 ¹³C NMR of AcO-PEG₂₇₋₃₇ (7) (100 MHz, CDCl₃)
**Fig. S137** $^1$H NMR of N$_3$-PEG$_{27}$-OH (8) (400 MHz, CDCl$_3$)

**Fig. S138** $^{13}$C NMR of N$_3$-PEG$_{27}$-OH (8) (100 MHz, CDCl$_3$)
Fig. S139 $^1$H NMR of N$_3$-PEG$_{27}$-OMs (9) (400 MHz, CDCl$_3$)

Fig. S140 $^{13}$C NMR of N$_3$-PEG$_{27}$-OMs (9) (100 MHz, CDCl$_3$)
Fig. S141 \(^1\)H NMR of N\textsubscript{3}-PEG\textsubscript{27}-N(Boc)\textsubscript{2} (10) (400 MHz, CDCl\textsubscript{3})

Fig. S142 \(^{13}\)C NMR of N\textsubscript{3}-PEG\textsubscript{27}-N(Boc)\textsubscript{2} (10) (100 MHz, CDCl\textsubscript{3})
Fig. S143 $^{13}$C NMR of N$_3$-PEG$_{27}$-NH$_2$ (100 MHz, CDCl$_3$)

Fig. S144 SEC of N$_3$-PEG$_{27}$-NH$_2$ (DMF, 1.00 mL/min, PS as standard)
Fig. S145 $^1$H NMR of Alkyne-PEG$_{27}$-Bn (11) (400 MHz, CDCl$_3$)

Fig. S146 $^{13}$C NMR of Alkyne-PEG$_{27}$-Bn (11) (100 MHz, CDCl$_3$)
Fig. S147 $^1$H NMR of Alkyne-PEG$_{27}$-OH (12) (400 MHz, CDCl$_3$)

Fig. S148 $^{13}$C NMR of Alkyne-PEG$_{27}$-OH (12) (100 MHz, CDCl$_3$)
Fig. S149 $^1$H NMR of Alkyne-PEG$_{27}$-OMs (13) (400 MHz, CDCl$_3$)

Fig. S150 $^{13}$C NMR of Alkyne-PEG$_{27}$-OMs (13) (100 MHz, CDCl$_3$)
Fig. S151 $^1$H NMR of Alkyne-PEG$_{27}$-N(Boc)$_2$ (14) (400 MHz, CDCl$_3$)

Fig. S152 $^{13}$C NMR of Alkyne-PEG$_{27}$-N(Boc)$_2$ (14) (100 MHz, CDCl$_3$)
Fig. S153 $^{13}$C NMR of Alkyne-PEG$_{27}$-NH$_2$ (100 MHz, CDCl$_3$)

Fig. S154 SEC of Alkyne-PEG$_{27}$-NH$_2$ (DMF, 1.00 mL/min, PS as standard)
Fig. S155 $^1$H NMR of mPEG$_{144}$-Mal (400 MHz, CDCl$_3$)