1. SUPPLEMENTAL ITEMS

Scheme S1. A hydrogel self-propagating cascade into a solution via degradation in preliminary test, Related to "Preliminary Test" in RESULTS AND DISCUSSION.
Figure S1. Kinetics experiments for the preliminary test results of Scheme S1, Related to “Preliminary Test” in RESULTS AND DISCUSSION. Butanethiol was exploited as the thiol trigger and it was conducted in pH 10 (borax/sodium hydroxide buffer). 3 was synthesized with Meldrum’s acid derivative 5 µmol and four-arm PEG azides 2.5 µmol. Rhodamine 6-G was added during the synthesis of 3. There were four samples 3 + 2-hydroxyethyl disulfide (BMEox) 5 µmol + butane thiol 0.5 µmol (0.1 equivalent), 3 + BMEox 5 µmol + butane thiol 1.5 µmol (0.3 equivalent), 3 + BMEox 5 µmol and only 3. (a) Absorbance spectra at 525 nm. (b) Fluorescence intensity at 555 nm. It was obtained by excitation at 470 nm. (c) Photograph showing changes of 3 from a hydrogel to a solution. (d) Optical changes of the first sample (3 + BMEox 5 µmol + butane thiol 0.5 µmol (0.1 equivalent)) with extracted solution. (e) Optical changes of the third sample (3 + BMEox 5 µmol) with extracted solution.
**Figure S2.** Absorption data of the preliminary test, Related to “Preliminary Test” in RESULTS AND DISCUSSION. (Figure S1a) (a) 3 + BMEox + butane thiol 0.1 equivalent, (b) 3 + BMEox + butane thiol 0.3 equivalent, (c) 3 + BMEox, (d) 3 were added in 5 ml of pH 10 buffer.
Figure S3. Fluorescence data of the preliminary test ($\lambda_{ex} = 470$ nm), Related to “Preliminary Test” in RESULTS AND DISCUSSION. (Figure S1b) (a) $3 + \text{BMEox + butane thiol 0.1 equivalent}$, (b) $3 + \text{BMEox + butane thiol 0.3 equivalent}$, (c) $3 + \text{BMEox}$, (d) $3$ were added in 5 ml of pH 10 buffer.
Table S1. Experimental results to find optimized conditions to obtain 5 from LC/MS data, Related to “Optimized Conditions and Rate Constant for the Thiol Trigger” in RESULTS AND DISCUSSION. The numbers in the table are the ratio (%) among the four products above. Between 0.5 and 1 hour, the yield of 5 did not significantly change. Due to the negligible yield difference between 0.5 and 1 hour, the 0.5 hour reaction time was adopted due to the relative speed to obtaining results.
Figure S4. Time kinetic studies to obtain 2nd order rate constant of model 1, related to Figure 1A. (a) Time kinetic studies with absorption changes of DCNP and 6 in acetonitrile in the presence of 2 equivalent of triethyl amine. (b) Time kinetic results for a concentration of 6 based on the absorption data spectra. 1, 2, 3, and 4 equivalents DCNP were added separately into acetonitrile in the presence of 6 (5 mM), and triethyl amine (10 mM). (c) First order rate constant was calculated from (b). Y-axis is $-kt$, so the slope is regarded as $-k$. (d) Second order rate constant was calculated with concentration of DCNP and the first order rate constant (c).
Figure S5. $^1$H NMR kinetic studies between DCNP and 6, Related to Figure 1A. There are 24 NMR results each and they were taken every 5 minutes for 2 hours. (a) 2 equivalents DCNP (20 mM) was added into acetonitrile-d in the presence of 6 (10 mM), and triethyl amine (20 mM). The disappearance of a was monitored over time. (b) 5 equivalents DCNP (50 mM) was added into acetonitrile-d in the presence of 6 (10 mM), and triethyl amine (20 mM).
Figure S6. Time kinetic studies to obtain 2nd order rate constant of model 1, Related to Figure 1B.
(a) Time kinetic studies with absorption changes of cyanide and 7 in acetonitrile. Cyanide was prepared from the mixture of potassium cyanide and 18-crown-6. (b) Time kinetic results for a concentration of 7 based on the absorption data spectra. 1, 2, 3, and 4 equivalents cyanide were added separately into acetonitrile in the presence of 7 (50 μM). (c) First order rate constant was calculated from (b). Y-axis is -kt, so the slope is regarded as -k. (d) Second order rate constant was calculated with concentration of cyanide and the first order rate constant (c).
Figure S7. Kinetics titration study at pH 10 buffer (borax/sodium hydroxide buffer), Related to “Titration Studies at pH 10 and 7.3” in RESULTS AND DISCUSSION. After reacting 4 (5 µmol), DCNP (0, 0.25, 0.5, and 1.5 µmol), and triethyamine (10 µmol) in acetonitrile for 30 minutes, the resulting mixture was added to the pH 10 buffer 5 mL in the presence of 2-hydroxyethyl disulfide (5 µmol) and 3. (a) Photos of the four samples with varying amounts of DCNP without Rhodamine 6G. The equivalent (eq.) is the ratio between the conjugate acceptor in 3 and DCNP: 0, 0.05, 0.1, and 0.3 (left to right). (b) Absorption data of time dependent titration for degradation of 3 with Rhodamine 6G. Absorption (525 nm) was measured by extracting 100 µL of each solution at intervals of 10 minutes for a total of 90 minutes.
Figure S8. Absorption data of time dependent titration for 3 degradation with different amount of DCNP in physiological pH (Phosphate-buffered saline), Related to Figure 2. 3 was synthesized with 5 µmol conjugate acceptor. After reacting 4 (5 µmol), DCNP ((a) none; (b) 0.25 µmol; (c) 0.5 µmol; (d) 1.5 µmol), and triethylamine (10 µmol) in acetonitrile for 30 minutes, the result mixture was added to the PBS 5 mL in the presence of BMEox (5 µmol) and 3. Absorption was measured by extracting 100 µL of the solution at intervals of 10 minutes for 200 minutes. The color of the graph over time was displayed in the order of rainbow colors: red, orange, yellow, green, blue, indigo, and purple. Where red is representative of the 10 minutes and purple is representative of the 200 minutes. The spectra changed in order according to the numbers and arrows in (b), (c), and (d).
Figure S9. Absorption data of time dependent titration for 3 degradation with different amount of DCNP in physiological pH, Related to Figure 2. After reacting 4 (5 µmol), DCNP ((a) none; (b) 0.25 µmol; (c) 0.5 µmol; (d) 1.5 µmol), and triethylamine (10 µmol) in acetonitrile for 30 minutes, the result mixture was added to the PBS 5 mL in the presence of BMeox (5 µmol) and 3 with R6G. Absorption was measured by extracting 100 µL of the solution at intervals of 20 minutes for 200 minutes. Where the red line is representative of the 10-minute interval and purple is representative of the 200-minute mark.
Figure S10. Nerve agents and their surrogates, Related to “Selectivity Test” in RESULTS AND DISCUSSION. DCNP (diethylcyanophosphonate) is a surrogate of a tabun, and both DFP (diisopropyl-fluorophosphate) and DCP (diethylchlorophosphate) are surrogates of a sarin and a soman. DSM (demeton-S-methyl) is employed as a surrogate of VX.
Figure S11. Selectivity test using UV-Vis spectroscopy, Related to “Selectivity Test” in RESULTS AND DISCUSSION. Absorption data of time dependent titration for 3 degradation with DCNP (a tabun mimic), DFP (a sarin and soman mimic), and Demeton-S-methyl (a VX mimic) in physiological pH (Phosphate-buffered saline). After reacting 4 (5 µmol), triethylamine (10 µmol), and (a) DCNP 0.5 µmol (0.1 equivalent); (b) DFP 5 µmol (1 equivalent); (c) DSM 5 µmol (1 equivalent) in acetonitrile for 30 minutes, the result mixture was added to the PBS 5 mL in the presence of 2-hydroxyethyl disulfide (5 µmol) and 3 with Rhodamine 6G (5 µmol). Absorption was measured by extracting 100 µL of the solution at intervals of 20 minutes for 240 minutes. (d) shows absorbance spectra of (a), (b), and (c) at 525 nm.
Figure S12. Selectivity test using LC-MS, Related to “Selectivity Test” in RESULTS AND DISCUSSION.
LC-MS data of the reaction 4 (10 mM) and triethylamine (20 mM) with (a) DCNP (10 mM); (b) DFP (10 mM); (c) DSM (10 mM) in acetonitrile for 90 minutes.
Figure S13. Membrane test of 3 via a cascade, Detailed version of Figure 3.  
(a) visualization for the kinetic samples designated 1, 2, 3, and 4 (left to right). Four different sets were made of 3 containing 5 µmol, 7 µmol, 9 µmol, and 11 µmol of the conjugate acceptor for samples 1, 2, 3, and 4, respectively. Each sample was made in a 1 dr vial, however, the reactants and solvent varied to make alter the thickness of the membrane. The conditions for each sample shown above was: 1. Meldrum’s acid linker (1.90 mg, 5 µmol, 1 equiv.), four-arm PEG azides (25 mg, 2.5 µmol, 0.5 equiv.), tert-butanol (50 µL), Milli-Q water (50 µL), sodium ascorbate (0.5 mg, 2.5 µmol, 0.5 equiv.), and copper sulfate (0.5 mg, 2 µmol, 0.4 equiv.), 2. Meldrum’s acid linker (2.66 mg, 7 µmol, 1 equiv.), four-arm PEG azides (35 mg, 3.5 µmol, 0.5 equiv.), tert-butanol (70 µL), Milli-Q water (70 µL), sodium ascorbate (0.7 mg, 3.5 µmol, 0.5 equiv.), and copper sulfate (0.7 mg, 2.8 µmol, 0.4 equiv.), 3. Meldrum’s acid linker (3.42 mg, 9 µmol, 1 equiv.), four-arm PEG azides (45 mg, 4.5 µmol, 0.5 equiv.), tert-butanol (90 µL), Milli-Q water (90 µL), sodium ascorbate (0.9 mg, 4.5 µmol, 0.5 equiv.), and copper sulfate (0.9 mg, 3.6 µmol, 0.4 equiv.), and 4. Meldrum’s acid linker (4.18 mg, 11 µmol, 1 equiv.), four-arm PEG azides (55 mg, 5.5 µmol, 0.5 equiv.), tert-butanol (110 µL), Milli-Q water (110 µL), sodium ascorbate (1.1 mg, 5.5 µmol, 0.5 equiv.), and copper sulfate (1.1 mg, 4.4 µmol, 0.4 equiv.). (b) Graphs comparing the height of samples 1, 2, 3, and 4 to the time the membrane starts to degrade. Each sample has the initial height of 40 mm.
Figure S14. STEM images before and after the membrane degradation, Related to Figure 4. (a) and (b) are scanning transmission electron microscope (STEM) images before (a) and after (b) the membrane degradation. Both scalebars are 100 nm.
2. SUPPLEMENTAL EXPERIMENTAL PROCEDURES

2.1. Materials

2.1.1. Cascade Materials
All materials were used as received unless otherwise stated. Meldrum’s acid was purchased from Oakwood Chemical. 6-Iodo-1-hexyne (97%), diethyl cyanophosphonate (DCNP), diisopropylfluorophosphate (DFP), O,O-Dimethyl S-2-(ethylsulfanyl)ethyl phosphorothioate (demeton-S-methyl), Dulbecco’s phosphate buffered saline, 2-hydroxyethyl disulfide, 4-mercaptophenol, tetrabutylammonium cyanide, Indium(III) acetate (In(ac)3, 99.99%), tin (IV) acetate (Sn(ac)4, >99.9%), oleic acid (OA, 90%, technical grade), oleyl alcohol (OleOH, 98%), KOH (>85%), sodium L-ascorbate (99%), potassium cyanide, 18-crown-6, and triethylamine (>99.9%) were all from MilliporeSigma. 4-(Methylthio)phenol was from Tokyo Chemical Industry. Four-arm poly(ethylene glycol) azide (> 95%, Mn = 10,000 Da) was purchased from JenKem Technology. CuSO4·5H2O was bought from Fisher Scientific. Borax / sodium hydroxide buffer solution pH 10 was purchased from Fluka. Other chemical reagents were purchased from MilliporeSigma, Acros Organics, Fisher Scientific and so on.
All cuvettes made by fused quartz were purchased from Starna Cells with standard screw and septum top.

2.1.2. Solid Phase Peptide Synthesis Materials
All solid phase peptide syntheses were completed using an automated microwave peptide synthesizer, CEM Liberty, at a 0.25 mmol scale. Unless otherwise stated, all of the following regents listed were used as received. The solvent, ACS grade dimethylformamide (DMF) was purchased from Fischer Scientific. Piperidine (99%) was purchased from Alfa Aesar. Ethyl(hydroxyamino)cyanoacetate (99.7%) was purchased from CHEM-IMPEX INT'L Inc. N, N’-Diisopropylcarbodiimide (99.5%) was purchased from CHEM-IMPEX INT'L Inc. The ACS grade acetic anhydride (99.7%) was purchased from Fisher Chemical. Fmoc-azidolysine (98%) was purchased from Novabiochem. The Fmoc-NH-PEG2-CH2CH2COOH (97%) was purchased from PUREPEG. Both the Fmoc-Asp(OtBu)-OH (98%) and Fmoc-Asp(OtBu)-Wang Resin (mesh:100-200, Subst.: 0.51 mmol/g) were purchased from P3BioSystems.

2.1.3. Solid Phase Click Reactions Materials
All the follow regents and solvents were used as received unless otherwise stated. The solvent, DMF, used for were purchased from Fisher Scientific. The 4-ethylbenzaldehyde (98%) was purchased from Ark Pharm, Inc. The 4-phenyl-1-butyn (97%) was purchased from Sigma Aldrich. Additionally, the copper (I) iodide (99%), and sodium L-ascorbate were both purchased from Sigma Aldrich. The synthesis of tris((1-benzyl-4-triazolyl)methyl)amine (TBTA) was accomplished following literature protocol.1

2.1.4. Solid Phase Peptide Synthesis Cleavage, Precipitation, and Purification Materials
Cleavage: Trifluoroacetic acid (99.9%) was purchased from CHEM-IMPEX INT'L Inc. and the triisopropylsilane (98%) was purchased from Aldrich Chemistry. Precipitation: The solvent, ACS grade ether, was purchased from Fisher Chemical. Precipitation: For the high-performance liquid chromatography (HPLC) both solvents methanol and nanopore water were altered by adding 0.1% formic acid. The formic acid (99%) was purchased by Acros Organics. Nanopure water is provided by The University of Texas at Austin. The Optima Methanol was purchased from Fisher Chemical.
2.2. Methods and Instruments

2.2.1. Nuclear Magnetic Resonance (NMR)
NMR spectra were recorded from The University of Texas at Austin NMR facility. Varian DirectDrive or Varian INOVA 400 MHz NMR spectrometers were employed on Synthesized compounds characterization. Time kinetics studies with NMR were recorded on Bruker AVIII HD 500 MHz cryoprobe. The NMR spectra were referenced to solvent and the spectroscopic solvents (CDCl₃, CD₃CN) were purchased from Cambridge Isotope Laboratories. All NMR spectral data was processed with the Mestrenova software package.

2.2.2. Liquid Chromatography-Mass Spectrometry (LC-MS)
Finnigan MAT-VSQ 700 and DSQ spectrometers were used to obtain mass spectra. LC-MS spectral data was acquired on an Agilent Technologies 6130 single quadrupole LC-MS using electrospray ionization.

2.2.2. High-Resolution Mass Spectrometry (HRMS)
High-resolution mass spec (HRMS) analysis was conducted by the University of Texas Mass Spectrometry Facility using Agilent Technologies 6530 Accurate Mass Q-TOF LC/MS system. MALDI-TOF MS analysis was performed using an AB-Sciex Voyager-DE PRO MALDI-TOF equipped with a 337 nm nitrogen laser in linear mode using CHCA as a matrix.

2.2.3. UV-Vis Spectroscopy
The UV-Vis absorbance spectra and kinetics were obtained in Cary 100 UV-Vis spectrophotometer from Agilent Technology. The spectra were run in Cary WinUV software: Scan, Kinetics and Scanning Kinetics, respectively.

2.2.4. Fluorescence Spectroscopy
Fluorescence spectra were recorded on a Photon Technology International Fluorescence Master fluorimeter. The source was a 75 W Xenon short arc lamp.

2.2.5. Solid Phase Peptide Synthesis, Purification, and Identification Equipment
The solid phase peptide synthesis was conducted via CEM Liberty Blue Microwave Peptide Synthesizer and all syntheses were done at the 0.25 mmol scale. Upon completion, HPLC was used to purify the desired product. The HPLC used was a Shimadzu Prominence system furnished with a Zorbax SB-C18 preparatory column (21.2 x 250 mm) with 7.0 µm packing material. The University of Texas at Austin Mass Spectrometry Facility used an Agilent Technologies 6530 Accurate Mass Q-TOF LC/MS for any high-resolution mass spectrometry (HRMS) data. A liquid chromatography mass spectrometry (LC-MS) instrument: Agilent Technologies 6125B Single Quadrupole LC-MS, was used to collect all UV-traces and MSD-TIC(+) data.

2.2.6. Scanning Transmission Electron Microscopy (STEM).
Samples were prepared by drop-casting dilute (0.1mg/mL) NC dispersions onto carbon-coated 400 mesh copper grids, with imaging performed on a Hitachi S5500 scanning transmission electron microscope (STEM) operating in the TEM mode with an accelerating voltage of 30 kV. Sizing NCs using the bright-field TEM images with the use of image j found NC sizes to be 9.8nm ± 3.5nm.²
2.3. Synthetic Procedures and Data

Synthesis of 5-(bis(hex-5-yn-1-ylthio)methylene)-2,2-dimethyl-1,3-dioxane-4,6-dione

To a flask in the presence of Meldrum’s acid (2 g, 13.9 mmol, 1 equiv.) in DMSO (10 mL) under argon gas, triethylamine (7.82 ml, 55.6 mmol, 4 equiv.) and carbon disulfide (0.84 mL, 13.9 mmol, 1 equiv.) were added in order. After stirring the mixture for 1 hour, 6-iodo-1-hexyne (4.59 mL, 34.75 mmol, 2.5 equiv.) was added to the mixture carefully. The resulting mixture was a clear dark red color and left to stir overnight. The solution was added over ice and extracted with dichloromethane. The organic phase was dried with magnesium sulfate and evaporated via rotary evaporation. The crude product was purified by a column chromatography with ethyl acetate/hexane (1/5, v/v) and yellow viscous oil was obtained (2.94 g, 56%). $^1$H NMR (400 MHz, CDCl$_3$) δ 3.18 – 3.04 (m, 4H), 2.21 (td, $J = 6.8$ Hz, 2.6 Hz, 2H), 1.95 (t, $J = 2.7$ Hz, 2H), 1.88 – 1.79 (m, 4H), 1.71 (s, 6H), 1.68 – 1.58 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 190.07, 160.04, 103.81, 103.14, 83.25, 69.25, 38.03, 27.52, 27.30, 26.92, 17.92; HRMS (ES+) m/z calc. for [M + Na]$^+$, 403.1008; found, 403.0996. See the reference 3.

Synthesis of Hydrogel (3)

To a 1 dr vial, 5-(bis(hex-5-yn-1-ylthio)methylene)-2,2-dimethyl-1,3-dioxane-4,6-dione (1.9 mg, 5 µmol, 1 equiv.), four-arm PEG azides (Mn = 10,000 g/mol, 25 mg, 25 µmol, 0.5 equiv.) and tert-butanol (50 µL) was added. Milli-Q water (35 µL) containing sodium ascorbate (0.5 mg, 2.5 µmol, 0.5 equiv.) was added to the mixture and stirred to give a homogeneous yellow solution using a vortexer and a sonicator. After dissolving the mixture completely, copper sulfate (0.5 mg, 2 µmol, 0.4 equiv.) in water (15 µL) was added and stirred for 1 minute with a vortexer. The mixture was stirred under a shaker for 1 hour. After removing the vial, a clear yellow hydrogel (3) was obtained. The hydrogel was purified in a neutral EDTA aqueous solution (10%) to extract the copper, remove sodium ascorbate and unreacted molecules. At last, 3 was ready to swell in water as a hydrogel. See the reference 3.
Synthesis of 4

\[
\begin{align*}
\text{HO-} & \quad \text{SH} & \quad \text{Ac}_2\text{O} & \quad \text{HO-} & \quad \text{S} \\
\text{4-Mercaptophenol} & & \text{Acetic anhydride} & & \text{Acetic anhydride} \\
1.252 \text{ g} & & 1.021 \text{ g} & & 1.021 \text{ g}
\end{align*}
\]

4-Mercaptophenol (1.252 g, 10 mmol), acetic anhydride (1.021 g, 10 mmol), and sodium acetate trihydrate (136.1 mg, 1 mmol) were stirred at room temperature (23-24 °C) overnight (12-18 hours). The mixture was extracted with dichloromethane in the presence of sodium bicarbonate. The organic phase was dried with magnesium sulfate and evaporated via rotary evaporation. The crude product was purified by a column chromatography with ethyl acetate/hexane (1/5, v/v) and the white powder was obtained (1.18 g, 71%). \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.20 (m, 2H), 6.73 (m, 2H), 6.08 (s, 1H), 2.42 (s, 3H). \(^13\)C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 197.90, 157.46, 136.23, 117.65, 116.72, 30.00; HRMS (-ESI) m/z calc. for [M - H], 167.0172; found, 167.0171.

Figure S15. \(^1\)H NMR spectrum of 4 (CDCl\textsubscript{3}).
Figure S16. $^{13}$C NMR spectrum of 4 (CDCl$_3$).

Figure S17. High resolution mass data of 4.
Synthesis of diethyl (4-(methylthio)phenyl) phosphate

Diethyl phosphorocyanidate (196 mg, 1.2 mmol) was added to a solution acetonitrile (8 mL) containing 4-(methylthio)phenol (126 mg, 1 mmol) and triethyl amine (202 mg, 2 mmol) at room temperature (23-24 °C). After stirring overnight (12-18 hours), the mixture was extracted with dichloromethane (DCM) and water with sodium bicarbonate. The organic phase was dried with magnesium sulfate and evaporated via rotary evaporation. The crude product was purified by a column chromatography with DCM/hexane (1/1, v/v) to DCM and the colorless clear liquid was obtained (236 mg, 85%).

$^1$H NMR (400 MHz, CD$_3$CN) δ 7.29 (d, $J$ = 8.7 Hz, 2H), 7.16 (d, $J$ = 8.9 Hz, 2H), 4.23 – 4.11 (m, 4H), 2.47 (s, 3H), 1.31 (t, $J$ = 7.0 Hz, 6H).

$^{13}$C NMR (101 MHz, CD$_3$CN) δ 148.49, 135.01, 127.91, 120.72, 64.60, 15.43, 15.34; HRMS (+ESI) m/z calc. for [M + Na]$^+$, 299.0477; found, 299.0475.

Figure S18. $^1$H NMR spectrum of 6 (CD$_3$CN).
Figure S19. $^1$H NMR spectrum of diethyl (4-(methylthio)phenyl) phosphate (CD$_3$CN).

Figure S20. $^{13}$C NMR spectrum of diethyl (4-(methylthio)phenyl) phosphate (CD$_3$CN).
Figure S21. High resolution mass data of diethyl (4-(methylthio)phenyl) phosphate.

### Synthesis of 7

4-Methoxythiophenol (701 mg, 5 mmol), acetic anhydride (510 mg, 5 mmol), and sodium acetate trihydrate trihydrate (680.4 mg, 5 mmol) were stirred at room temperature (23-24 °C) overnight (12-18 hours). The mixture was extracted with dichloromethane in the presence of sodium bicarbonate. The organic phase was dried with magnesium sulfate and concentrated using rotary evaporation. The crude product was purified by column chromatography with ethyl acetate/hexane (1/20, v/v) and the colorless clear liquid was obtained (756 mg, 83%). ¹H NMR (400 MHz, CDCl₃) δ 7.32 (d, J = 8.9 Hz, 2H), 6.94 (d, J = 9.0 Hz, 2H), 3.81 (s, 3H), 2.39 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 195.15, 160.68, 136.09, 118.70, 114.88, 55.33, 29.94; HRMS (+ESI) m/z calc. for [M + Na]⁺, 205.0294; found, 205.0296.
Figure S22. $^1$H NMR spectrum of 4-methoxybenzenethiol (CD$_3$CN).

Figure S23. $^1$H NMR spectrum of 7 (CDCl$_3$).
Figure S24. $^{13}$C NMR spectrum of 7 (CDCl$_3$).

**Target Compound Screening Report**

Results Acquired by The University of Texas at Austin Mass Spectrometry Facility

| Data File          | MGF20-1102(Doshee_7)_hrESIws.id | Sample Name  | 1102(Doshee_7) | Comment | 1102(Doshee_7) |
|--------------------|---------------------------------|---------------|----------------|---------|----------------|
| Position           | FIA-MS                          | Instrument Name | Instrument 1 | User Name | Instrument 1 |
| Acq Method         | FIA_pro.m                       | Acquired Time  | 16/12/2005 3:29:06 PM | DA Method | 45.m          |

**HS Zoomed Spectrum**

Cpd 1: C9 H10 O2 S; +ESI Scan (0.29-0.39 min, 7 Scans) Frag=80.0V MGF20-1102(Doshee_7)_hrEIw.

**HR Spectrum Peak List**

| Mass (m/z) | Charge | Abundance | Formula       | Ion Species | Tg Mass Error (ppm) |
|------------|--------|-----------|---------------|-------------|---------------------|
| 205.0296   | 1      | 100.0000  | C9H8O2S      | Ph=H=H      | -0.20               |
| 206.0329   | 1      | 102.0009  | C9H8O2S      | Ph=H=H      | 0.36                |
| 207.0276   | 1      | 95.0000   | C9H8O2S      | Ph=H=H      | -0.20               |
| 208.0307   | 1      | 95.0000   | C9H8O2S      | Ph=H=H      | 0.36                |

**End Of Report**

Figure S25. High resolution mass data of 7.
Microwave Assisted Peptide Synthesis
Using the peptide synthesizer, the ligands were made using standard Fmoc-deprotection using piperidine and the desired natural or unnatural amino acid, and PEG were coupled using diisopropylcarbodiimide (DIC)/Ethyl(hydroxyamino)cyanoacetate (Oxyma) amide coupling conditions. The ligands were synthesized using Wang resin. The microwave assisted peptide synthesizer coupled the amino acids with DIC/Oxyma in two steps: 1) 75 °C, 170 W for 15 seconds, and 2) 90 °C, 30 W for 110 seconds. All Fmoc-deprotections were completed using a piperidine/DMF (20:100) solution in two phases: 1) 75 °C, 155 W for 15 seconds, and 2) 90 °C, 30 W for 50 seconds. Following the same standard synthesis procedures, the N-terminus of the ligand was deprotected and capped with acetic anhydride. All resins were sequentially washed with DMF (25 mL), DCM (25 mL), and MeOH (25 mL). The resin was dried under vacuum for at least three hours prior to the solid phase copper (I)-catalyzed alkyne-azide cycloaddition reaction.

Solid Phase Copper(I)-Catalyzed Alkyne-Azide Cycloaddition
Solid Phase Copper(I)-Catalyzed Alkyne-Azide Cycloaddition (SP-CuAAC), was preformed using the following described procedure to install the desired alkyne (4-phenyl-1-butyne or 4-ethynlbenzaldehyde) onto the azide of the ligand. The resin was transferred to a 20 mL dram vial and suspended in 4 mL of DMF. With 1.1 equivalencies (azide/alkyne, 1:1.1), the desired alkyne was added to the vial. The vial was then sealed and degassed with N₂ gas. The catalyst solution was made in a separate vial under inert conditions. The catalyst was prepared by combining tris(1-benzyl-4-triazolylmethyl)amine (TBTA)/sodium ascorbate/copper iodide (0.4: 0.4:0.2 eq.) and dissolving the solids in a total of 3.4 mL of DMF and 1.6 mL of H₂O. The catalyst solution was added to the dram vial containing the resin and alkyne and the solution was equipped with a N₂ balloon. The resulting mixture was left on a shaker for 12-24 hours at room temperature. Once completed the resin was washed with DMF (40 mL), DCM (40 mL), and MeOH (40 mL). The resin was left to dry under vacuum for at least four hours prior to cleaving the ligand off the resin. Once the resin was dried the ligand was cleaved off the resin. For the resin that was subjected to the SP-CuAAC with 4-ethynlbenzaldehyde, the cleavage solution consisted of TFA/H₂O (90:10). For the resin that was subjected to the SP-CuAAC with 4-phenyl-1-butyne, the cleavage solution consisted of TFA/TIS/H₂O (95:2.5:2.5). In both cases the resin was agitated for 2.5-3 hours with their respective cleavage solution. The cleavage solution was removed, and the ligand was precipitated with ether. Upon removal of the ether, the precipitant was analyzed using an LCMS (5% to 95% MeOH gradient over 12 minutes, MeOH/H₂O binary system) to display the desired products. The peaks in the LCMS were identified using MS. Further purification using a HPLC (gradient: isocratic binary system, MeOH/H₂O 10% to 95% over 90 minutes, both the MeOH and H₂O were altered with 0.1% formic acid) removed residual biproducts. The desired ligand was collected and the MeOH was removed using a rotatory evaporation. The residual water was lyophilized to yield a white powder for all ligands made.
Benzyl-Ligand

Yield: 87.93 mg (98.5 µmol), 11.3%, white solid. HRMS(+ESI)/ Da: M = C_{40}H_{60}N_{8}O_{15}, (M+Na)^{+}\text{theoretical} = 915.4076, (M+Na)^{+}\text{observed} = 915.4070, Target Mass Error = -0.72 ppm.

Figure S26. The benzyl-ligand purity conformation via LC-MS. (a) The UV-trace at both 240 and 214 nms over a 12 minutes (LCMS Trace: 5% to 95% MeOH gradient) displays only one peak. (b) The MSD-TIC (+) of the single peak shown in (a) displaying the mass of the desired ligand.
Figure S27. The LCMS-trace of the benzyl-ligand prior to HPLC purification. (a) The crude UV-trace of the benzyl-ligand at 240 and 214 nm. (b) The identities of known impurities.
Aldehyde-Ligand

Yield: 105.45 mg (118.1 µmol), 12.0%, white solid. HRMS(+ESI)/ Da: M = C_{39}H_{56}N_{8}O_{16}, (M+Na)^+ theoretical = 915.3712, (M+Na)^+ observed = 915.3706, Target Mass Error = -2.49 ppm.

Figure S28. The Aldehyde-ligand purity conformation via LC-MS. (a) The UV-trace at both 240 and 214 nms over a 12 minutes (LCMS Trace: 5% to 95% MeOH gradient) displays only one peak. (b) The MSD-TIC (+) of the single peak shown in (a) displaying the mass of the desired ligand.
Figure S29. The LCMS-trace of the Aldehyde-ligand prior to HPLC purification. (a) The crude UV-trace of the Aldehyde-ligand at 240 and 214 nm. (b) The identities of known impurities.
Synthesis of Colloidal nanocrystals (NCs)
Colloidal nanocrystals (NCs) were synthesized by the modification of a slow injection method to synthesize monodispersed spheres. A metal precursor solution (4.75 mmol In(III)acetate, 0.25 mmol Sn(IV)acetate, 10 mL oleic acid) was slow injected into 13 mL of oleyl alcohol held at 290 °C under inert atmosphere. After the reaction, NCs were washed five times with ethanol and redispersed in hexane. NCs were functionalized using a direct ligand exchange method. Oleate-capped NCs in hexane were again flocculated with ethanol and introduced to polar ligand solution (0.01 M ligand in DMF) and sonicated (15 mins). NCs were then flocculated using an ethanol:hexane (1:1) mixture and introduced to a basic solution of water (0.1M KOH pH 14) sonicated (15 mins). The NC precipitate was then centrifuged and dispersed with a second basic solution (TEA pH 12) and sonicated for (15 mins). The NCs were centrifuged using a filtered centrifuged tube for spin dialysis and redispersed in pure water maintain some basicity (5mL pH 10). Particles were characterized using ¹H NMR, UV/Vis, and STEM.

Figure S30. Absorbance data of NCs and triethylamine (TEA).
Figure S31. $^1$H NMR spectrum of NCs.
3. SUPPLEMENTAL REFERENCES

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