

## Supplementary Information

Geared Photochemistry: Interdependent Heterogeneous Near-Infrared  
Catalytic System Using Up-Conversion Glass and g-CN for CuAAC  
Chemistry

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## **References**

## 1. Materials

Erbium(III) oxide ( $\text{Er}_2\text{O}_3$ , ChemPur, 99.9%), tellurium(IV) oxide ( $\text{TeO}_2$ , Alfa Aesar, 99.95%), zinc oxide ( $\text{ZnO}$ , ChemPur, 99.9%), ytterbium(III) nitrate pentahydrate ( $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ , Aldrich, 99.9%), thulium(III) oxide ( $\text{Tm}_2\text{O}_3$ , Alfa Aesar, 99.9%) were used as purchased.

2,4-diamino-6-phenyl-1,3,5-triazine (97%, Sigma Aldrich), 4-methyl-5-vinylthiazole (vTA, 97%, Sigma Aldrich), cyanamide (Sigma Aldrich), cyanuric acid (98%, Sigma Aldrich), ethanol (99.5%, Kanto chemi-cals),  $\text{NH}_4\text{HF}_2$  in water (4 M, 95%, Wako Chemicals),  $\text{SiO}_2$  particles in water (Ludox HS-40, Sigma Aldrich) were used as purchased.

Benzyl bromide (Merck, 98%), 9-hydroxymethylanthracene (Alfa Aesar, 97%) phenyl acetylene (Sigma, 98%), propargyl alcohol (Sigma, 95%), propargyl amine (Sigma, 98%), 3-ethynylthiophene (Sigma, 98%), ethyl 2-bromopropionate (Sigma, 98%), d-dimethyl sulfoxide, ( $\text{DMSO-d}_6$ , Merck), sodium azide ( $\text{NaN}_3$ , Panreac), N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA, Aldrich), ethyl  $\alpha$ -bromoisobutyrate (Aldrich, 98%), copper(II) chloride ( $\text{CuCl}_2$ , Merck) and copper (I) bromide ( $\text{CuBr}$ , Alfa Aesar) were used as received. Styrene (Merck) was purified by using a basic alumina column to remove the inhibitor and then stored in the fridge.  $\epsilon$ -Caprolactone (Merck), and stannous octoate (Aldrich) were dried with  $\text{CaH}_2$  under vacuum.

## 2. Instrumentation & Characterization

Absorption measurement of co-doped tungsten-tellurite glass was recorded using Shimadzu UV-VIS-NIR 3101 PC spectrometer between 300-2000 nm at room temperature. Upconversion (UC)-emission spectra of the co-doped zinc-tellurite glass were collected between 400-850 nm wavelength region using a monochromator (Princeton Instruments, model SP2500i), a diode laser operating at 975 nm as an excitation source (CNI MDL-H-975 Model), and a detector (SI 440 Acton series) for the detection of the luminescence in the visible region. Power meter (Coherent Field Max II - TOP Model) was used to measure the output power of the laser beam. The International Commission on Illumination (CIE-1931) (Commission Internationale de l'éclairage) coordinates of the obtained UC-emission was measured using an illuminance meter (AsenseTek Lighting Passport).

FT-IR spectra of graphitic carbon nitride (g-CN) powders were recorded on a PerkinElmer FTIR Spectrum One spectrometer. Scanning electron microscopy (SEM) was performed using

JSM-7500F (JEOL). The structures of materials were examined by transmission electron microscopy (TEM) using an EM 912 Omega microscope at 120 kV. Photoluminescent emission spectra in powder forms were recorded on Jasco FP-8300 instrument at ambient temperature with the excitation wavelength at 360 nm. Porosimetry was performed using Quantachrome Quadrasorb instrument with N<sub>2</sub> gas after samples were degassed at 100 °C overnight. Surface areas and pore volumes of the samples were estimated via the Brunauer–Emmett–Teller (BET) method.

<sup>1</sup>H-NMR (500 MHz) spectra were recorded in deuterated dimethyl sulfoxide (DMSO-d<sub>6</sub>) with tetramethylsilane as an internal standard on Agilent VNMRS500 spectrometer at 25 °C.

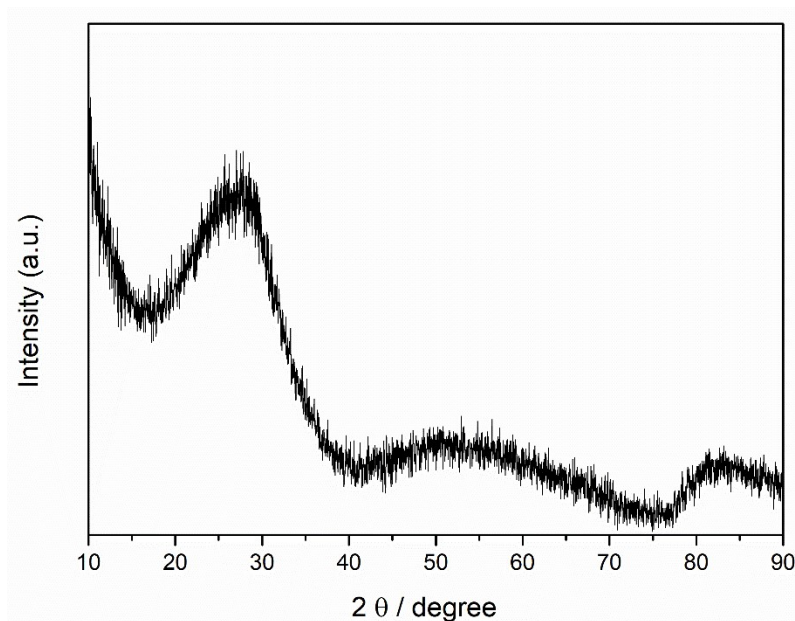
### 3. Experimental Section

#### Synthesis of Up-conversion Glass

Zinc-tellurite glass doped with Yb<sup>3+</sup> and Tm<sup>3+</sup> ions were synthesized by the conventional melt quenching method for emitting blue up-conversion. The composition of the glass was (80%) TeO<sub>2</sub> + (17.25%) ZnO + (2.5%) Yb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O + (0.25%) Tm<sub>2</sub>O<sub>3</sub> moles. High purity of (at least 99.99%) TeO<sub>2</sub>, ZnO, Yb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and Tm<sub>2</sub>O<sub>3</sub> powders were mixed in an agate mortar. Mixed powders were melted in a platinum crucible in an electric furnace at 950 °C for 1 hour and poured on a stainless steel template which is pre-heated 150 °C below the glass transition temperature. As-cast glass was annealed on the stainless steel template for 2 hours to relieve internal stresses. The detailed synthetic method was described in some previous works<sup>1</sup>.

Glasses are formed by the rapid quenching of the liquid to form a solid. If the cooling is sufficiently rapid to prevent crystallization or phase separation, the resulting solid is disordered when compared to the crystalline state. The disorder in a network of a glass structure does not have a translational periodicity and hence suffers from the lack of a long-range order (LRO) that is observed in crystalline solids. However, the existence of a strong bonding between the neighboring atoms results in a well-defined short-range order (SRO) in the glass network. The SRO due to chemical bonding may be defined in terms of the coordination number of the central atom, the nearest bond length and the bond angle. The glass forming range of TeO<sub>2</sub>-ZnO glass varies from 2.5 to 45 mol% with an average glass density of 5.602g/cm<sup>3</sup>. The atomic arrangement in 80 mol% TeO<sub>2</sub> – 20 mol% ZnO shown in Figure 1 that the atomic distances are most sensitive to the glassy state due to the fact that the shortest Te–Te distance in α-TeO<sub>2</sub> is 3.76 Å. This relatively long distance between the two heavy metal cations suggests that some weak metal bonds are present. When the ion radius (r) and bond energy of TeO<sub>2</sub> and SiO<sub>2</sub> (a

common glass former) glass formers are compared, it was found that Te atoms have the greatest  $r$  and mass, the highest value of the average Te–O distance, and the lowest Te–Te bond energy<sup>2</sup>

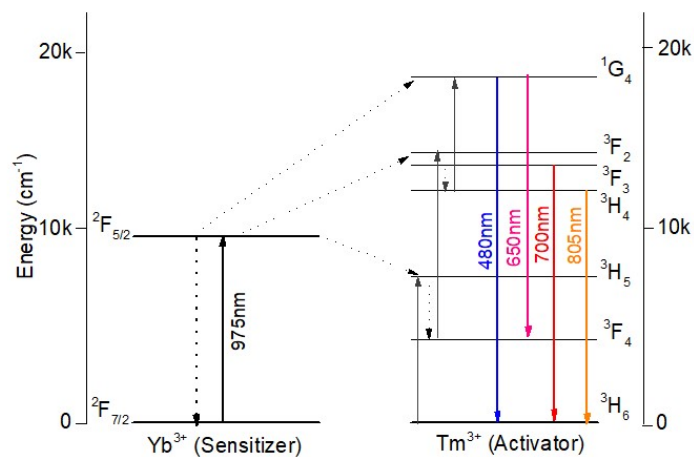


**Figure S1.** X-Ray Diffraction of up-conversion glass

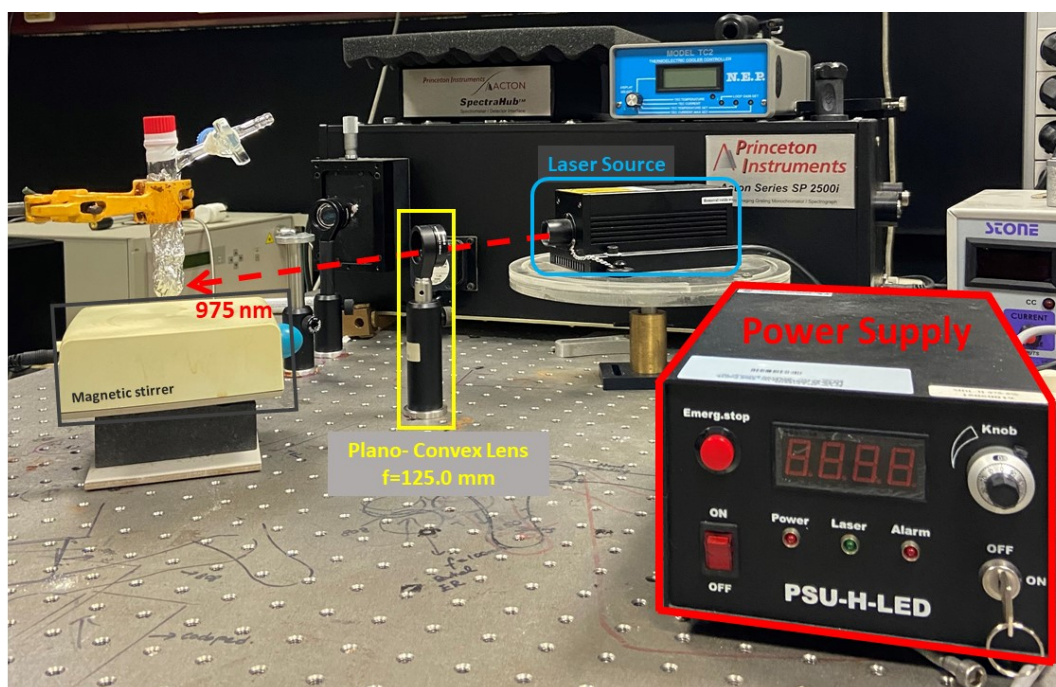
### The Energy Level Diagram of Yb<sup>3+</sup> and Tm<sup>3+</sup> Ions

Energy level diagram of Yb<sup>3+</sup> and Tm<sup>3+</sup> ions illustrated in figure S1 presents possible ways of energy transfer processes from Yb<sup>3+</sup> to Tm<sup>3+</sup> ions upon 975 nm laser excitation. The excited Yb<sup>3+</sup> ions into their excitation state after the absorption of the laser light enhance the population of all the energy levels by transferring their absorbed energy to the activator, Tm<sup>3+</sup> ions. Intensity dependence of the blue and red UC emissions on the excitation energy of 975nm laser light tells us that both the red and blue light emissions occur with the aid of the two excited Yb<sup>3+</sup> ions. In this process, excited Yb<sup>3+</sup> ion-pair transfer their energy to a nearby Tm<sup>3+</sup> ion in its ground state. As a result, Tm<sup>3+</sup> ion initially in its ground state is excited into the <sup>1</sup>G<sub>4</sub> level from where the blue light emission occurs via <sup>1</sup>G<sub>4</sub>→<sup>3</sup>H<sub>6</sub> transition. When the energy transfer occurs between the <sup>2</sup>F<sub>5/2</sub> level of Yb<sup>3+</sup> ions to the <sup>3</sup>H<sub>5</sub> level of Tm<sup>3+</sup> ions, blue emission occurs. Thereafter, the electrons in the <sup>3</sup>H<sub>5</sub> level decay to the <sup>3</sup>F<sub>4</sub> level non-radiatively through multi-phonon relaxation processes. Subsequently, excited Yb<sup>3+</sup> ions can populate higher <sup>3</sup>F<sub>2</sub> and <sup>3</sup>F<sub>3</sub> electronic energy states from <sup>3</sup>F<sub>4</sub> level of Tm<sup>3+</sup> ions via second energy transfer, and afterwards, by a non-radiative relaxation process, <sup>3</sup>H<sub>4</sub> level is populated. Finally, <sup>1</sup>G<sub>4</sub> level is populated via a third energy transfer, and then <sup>1</sup>G<sub>4</sub> → <sup>3</sup>H<sub>6</sub> (blue) and <sup>1</sup>G<sub>4</sub> → <sup>3</sup>F<sub>4</sub>, <sup>3</sup>F<sub>2,3</sub> → <sup>3</sup>H<sub>6</sub> (red) emissions occur. The blue emission originating from the <sup>1</sup>G<sub>4</sub> level of Tm<sup>3+</sup> ions occurs through three-step

energy transfer from  $\text{Yb}^{3+}$  to  $\text{Tm}^{3+}$  and as well as the excitation of the  $^1\text{G}_4$  level of  $\text{Tm}^{3+}$  ions via cooperative excitation of the  $\text{Yb}^{3+}$  - ion pair that involves a two-step photon absorption process. The intensity of the emitted light was measured between  $100 (\pm 5) \text{ mW/cm}^2$ .



**Figure S2.** The schematic representation of energy level diagram of  $\text{Yb}^{3+}$ , and  $\text{Tm}^{3+}$  ions.



**Figure S3.** The photography of laser set-up.

### **Synthesis of mpg-CN**

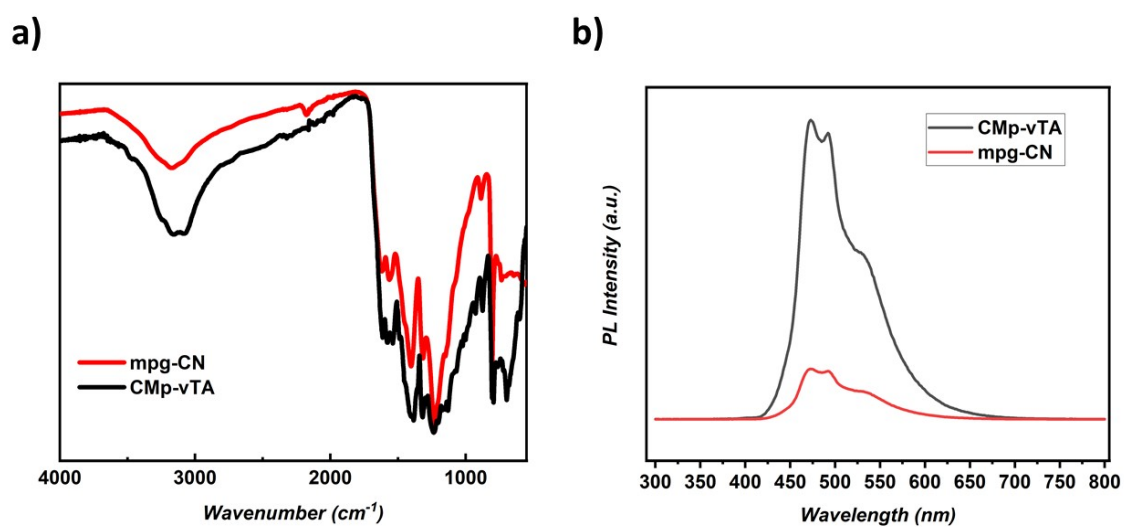
According to the literature, a unity mass ratio of silica to cyanamide was used to synthesize g-CN. Cyanamide (20 g) was dissolved in a 40 wt.% dispersion of 12 nm SiO<sub>2</sub> particles in water (50 g) with stir-ring at 80 °C for about 3 h to evaporate the water. The resulting white powder was then heated under N<sub>2</sub> atmosphere at a rate of 2.3 K min<sup>-1</sup> over 4 h to reach a temperature of 550 °C, and then held at this temperature for an additional 4 h. The resulting brown-yellow powder was stirred in 200 mL of 4 M NH<sub>4</sub>HF<sub>2</sub> for 2 h, followed by filtration and washing with 100 mL of H<sub>2</sub>O and 50 mL of ethanol. This washing cycle was repeated to completely remove the silica template. The powder was then stirred in 200 mL of H<sub>2</sub>O for 2 h, then filtered and washed with H<sub>2</sub>O and ethanol. Finally, the powders were dried at 120 °C overnight.

### **Synthesis of CMp-vTA**

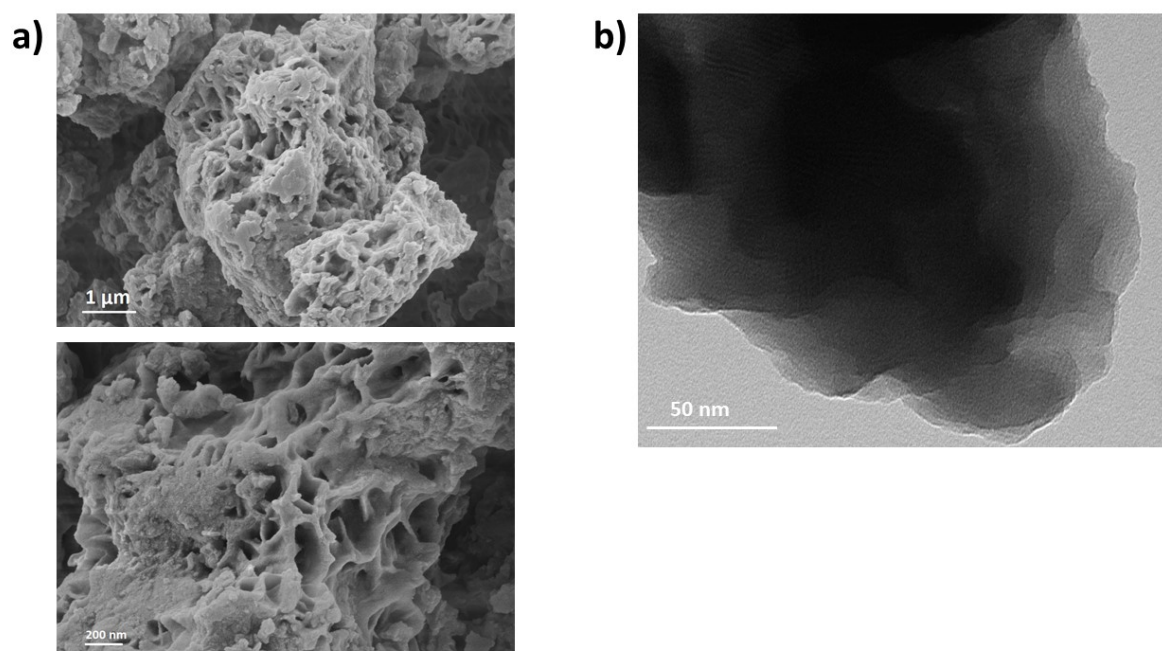
CMp-vTA particles were synthesized according to the cited literature. 100 mg CMp (carbon nitride made from cyanuric acid: 2,4-diamino-6-phenyl-1,3,5-triazine comonomers at 450 °C) was mixed with 1 ml vTA and sonicated for 5 min in a sonic bath. Mixture was degassed with nitrogen flux for 10 min and placed between 2 50 W LEDs and stirred for 3 h under continuous visible light irradiation and for purification, the mixture was filtered and washed with ethanol 3 times (20 ml each portion) and dried under vacuum at 60°C overnight. After cooling to ambient temperature, dark-yellow CMp-vTA powder was obtained and well grinded before usage.

**Table S1.** Specific surface area and pore volumes of CMp-vTA and mpg-CN powders obtained via porosimetry (BET).

	Specific Surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)
CMp-vTA	12.33	0.105
mpg-CN	165.55	0.372

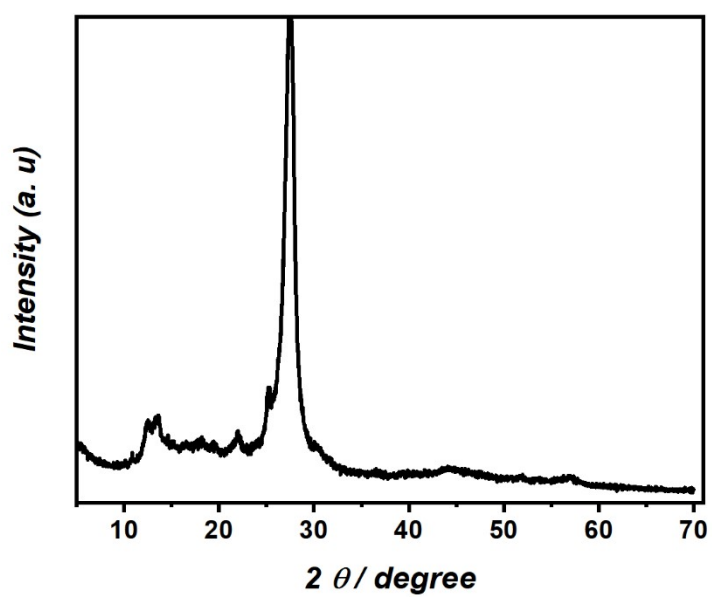


**Figure S4.** A) FT-IR and B) PL spectra of mpg-CN and CMp-vTA powders.

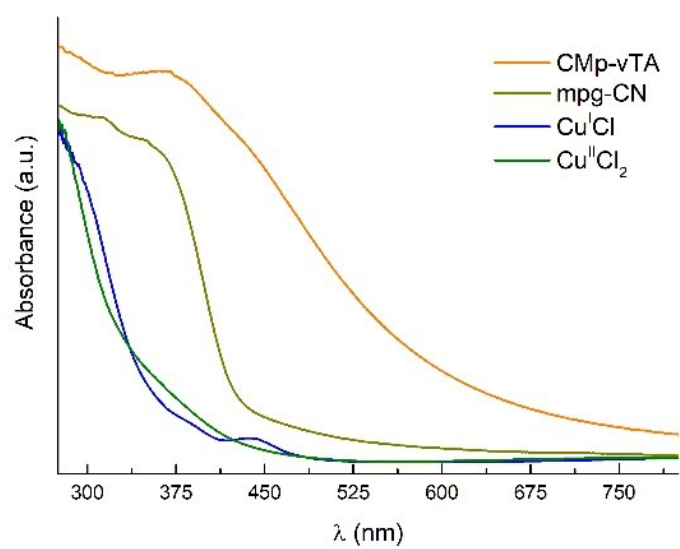


**Figure S5.** A) SEM images and B) TEM image of CMp-vTA.





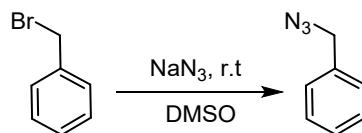
**Figure S6.** X-Ray Diffraction of graphitic carbon nitride



**Figure S7.** UV-Vis spectra of copper salts, CMp-vTA, and mpg-CN.

## Synthesis of Azide & Alkyne Functional Molecules

### Benzyl azide

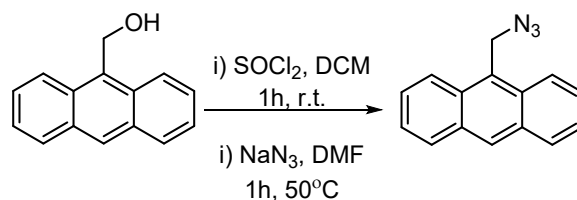


Benzyl azide was synthesized according to the previous study <sup>4</sup>. Benzyl bromide (5 mL, 1 eq.) was dissolved in 200 mL DMSO and NaN<sub>3</sub> (1.2 eq.) was added slowly to the reaction. After the given time 100 mL diluted water was introduced to the reaction and allowed to cool down to room temperature. The solution was extracted with Et<sub>2</sub>O (3 x 100 mL). The organic layer was washed with water (100 mL), the brine (100 mL) and then dried over Mg<sub>2</sub>SO<sub>4</sub>, respectively. The solution was filtered and the solvent was removed under reduced pressure. The pale yellow product was obtained with yield of 96% and characterized by <sup>1</sup>H NMR and FT-IR.

<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 7.4–7.3 (m, 5H, -C<sub>6</sub>H<sub>5</sub>), 4.4 (s, 2H, -CH<sub>2</sub>-N<sub>3</sub>).

FTIR: 2108 cm<sup>-1</sup>.

### 9-(Azidomethyl)anthracene

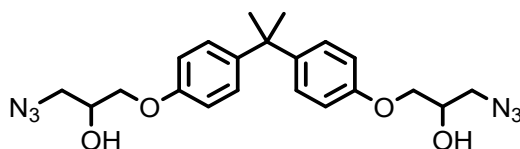


Benzyl azide was synthesized according to the previous study <sup>4</sup>. 9-Hydroxymethylanthracene (1.54 g, 7.4 mmol) was dissolved in DCM (50 mL) and cooled to 0 °C. Then, SOCl<sub>2</sub> (1.5 eq.) was slowly added to the solution and allowed to warm up to room temperature while being stirred for 1 h. The solvent was evaporated under vacuum and the residue was dissolved in DMF (10 mL) and then NaN<sub>3</sub> (1.5 eq.) was added, and the reaction was stirred at 50 °C for 1 h. The mixture was extracted with EtOAc and the organic phases were washed with brine, dried with anhydrous MgSO<sub>4</sub>. The solution was filtered and concentrated under a reduced vacuum. The spectral data is similar as previous study<sup>4</sup>.

<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 8.7 (s, 1H), 8.4 (dd, 2H), 8.1 (dd, 2H), 7.6 (td, 2H), 7.5 (td, 2H), 5.51 (s, 2H)

$^{13}\text{C}$  NMR (DMSO- $d_6$ , 125 MHz)  $\delta$  131.3, 130.7, 129.5, 129.0, 127.2, 126.9, 125.8, 124.5, 45.9

### Synthesis of bisphenol A di(3-azido-2-hydroxy propan-1-ol) ether (Az-1)

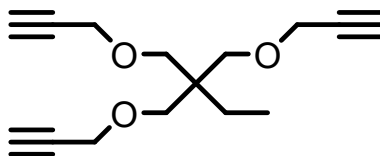


A literature procedure was followed <sup>5</sup>. The synthesis steps follow exactly the ones in the literature. Bisphenol A di(3-azido-2-hydroxy propan-1-ol) ether as light yellowish viscous oil was directly used without further purification. (Yield 97%)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 Hz)  $\delta$  7.15 (m, 4H), 6.82 (m, 4H), 4.16 (m, 2H), 4.0 (dd, 4H), 3.51 (m, 4H), 1.65 (s, 6H)

$^{13}\text{C}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  131.38, 130.67, 129.51, 129.09, 127.26, 126.83, 125.80, 45.93.

### Synthesis of 1-(prop-2-yn-1-yloxy)-2,2-bis((prop-2-yn-1-yloxy)methyl) butane (Alk-1)



A literature procedure was followed <sup>6</sup>. The synthesis steps follow exactly the ones in the literature. The crude product was then purified using column chromatography to obtain a clear oil. (Yield 72%)

$^1\text{H}$  NMR (500 Hz, DMSO- $d_6$ )  $\delta$  0.80 (t, 3H, CH<sub>3</sub>), 1.30 (2H, q, CH<sub>2</sub>-CH<sub>3</sub>), 3.30 (s, 6H, CH<sub>2</sub>), 4.10 (d, 6H, CH<sub>2</sub>-Alkyne).

$^{13}\text{C}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  7.84 (1C, CH<sub>3</sub>), 23.33 (1C, CH<sub>2</sub>), 42.82 (1C, C), 58.39 (3C, CH<sub>2</sub>-Alkyne), 70.13 (3C, CH<sub>2</sub>), 77.24 (3C, CH<sub>2</sub>), 80.83 (3C, C, alkyne).

### $\omega$ -azido terminated polystyrene (PS- $\text{N}_3$ )

$\omega$ -Bromo functional polystyrene was synthesized by atom transfer radical polymerization. The controlled polymerization took place via the standard Schlenk technique with a glass vacuum manifold connected to an inlet of nitrogen. The reactants used for classic polymerization reaction are as follows: Styrene (3 mL, 0.026 mol), CuCl (38 mg, 0.26 mmol), PMDETA (0.56  $\mu\text{L}$ , 0.26 mmol), and EBiB (39  $\mu\text{L}$ , 0.26 mmol). The tube was sealed and degassed using three

freeze-pump-thaw cycles. After cool down to the room temperature, the reaction was placed in 110 °C oil bath. After 15 min. the reaction was ended and the solution was diluted with THF. Lately, the solution was passed through out the basic alumina and concentrated to precipitate into methanol. The precipitated polymer was filtered and dried under high vacuum overnight.  $M_{n, GPC}$ : 1917 g·mol<sup>-1</sup>,  $M_{w, GPC}$ : 2200 g·mol<sup>-1</sup>, Đ: 1.1

In a flask equipped with a magnetic stirrer, PS-Br (200 g, 0.1 mmol) and NaN<sub>3</sub> (6.8 mg, 0.5 mmol) were dissolved in 3 mL DMF. The reaction mixture was stirred overnight at room temperature, then precipitated in 10-fold excess of methanol, filtered and dried in vacuum to yield PS-N<sub>3</sub>. Yield 95%

FTIR: 2096 cm<sup>-1</sup>.

### **Acetylene-terminated poly( $\epsilon$ -caprolactone) (PCL-Alkyne)**

To a Schlenk tube, Propargyl alcohol was dissolved in  $\epsilon$ -caprolactone and heated to 110 °C under nitrogen. After the reaction mixture warmed up homogeneously, one drop of tin octoate was added to the reaction media and the solution was stirred for 3 hours. The obtained polymer precipitated in methanol to yield PCL-Alkyne. White solid, (80%).

$M_{n, GPC}$ : 4266 g·mol<sup>-1</sup>,  $M_{w, GPC}$ : 6215 g·mol<sup>-1</sup>, Đ: 1.2.

FTIR: 2102 cm<sup>-1</sup>.

## **Photoinduced Copper Catalyzed Azide-Alkyne Cycloaddition Reaction**

### **Photoinduced CuAAC Reactions**

All reactions were conducted in Schlenk tube under nitrogen atmosphere. In a typical procedure, 10 mg g-CN and the piece of UCG were placed in 1 mL DMSO-d<sub>6</sub> and azide compound (1 mmol), CuCl<sub>2</sub> (0.05 mmol), PMDETA (0.1 mmol) were added to the tube. After the given time alkyne compound (1 eq.) was added to the reaction media. Then the tube was placed on a stir bar which is equipped with laser light source (refer to the Supplementary Movie 1).

### **End group modification via photoinduced CuAAC Reaction**

The end group functionalization reaction of poly( $\epsilon$ -caprolactone) with azide functional anthracene was conducted in a 10 mL Schlenk tube. Alkyne functional PCL was dissolved in 2 mL DMF. After the clear solution was obtained, CuCl<sub>2</sub> (1 eq.) and PMDETA (1 eq.) were added

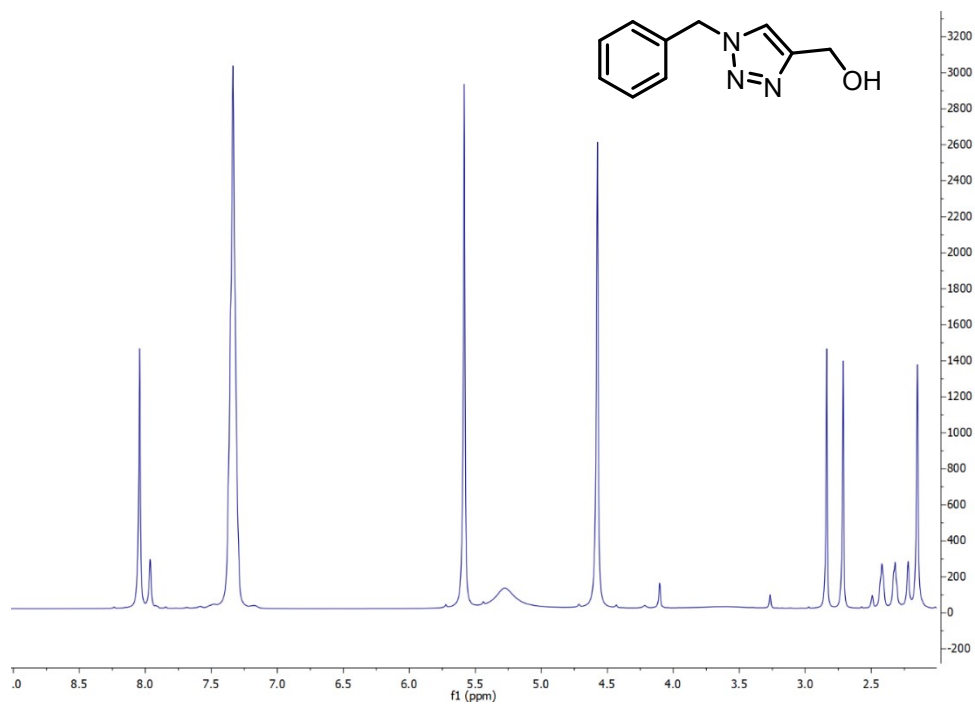
to the tube and allowed to stir. After 5 min., azide functional anthracene was added to the reaction media and the Schlenk tube was sealed. The tube was directly placed into the laser source equipped with a stir bar. After the given time, the solution was throughout the column to remove the copper complex and the solution was concentrated. The concentrated solution was precipitated into excess methanol then the polymer was collected and dried under a high-pressure vacuum overnight.

### **Block Copolymer Formation**

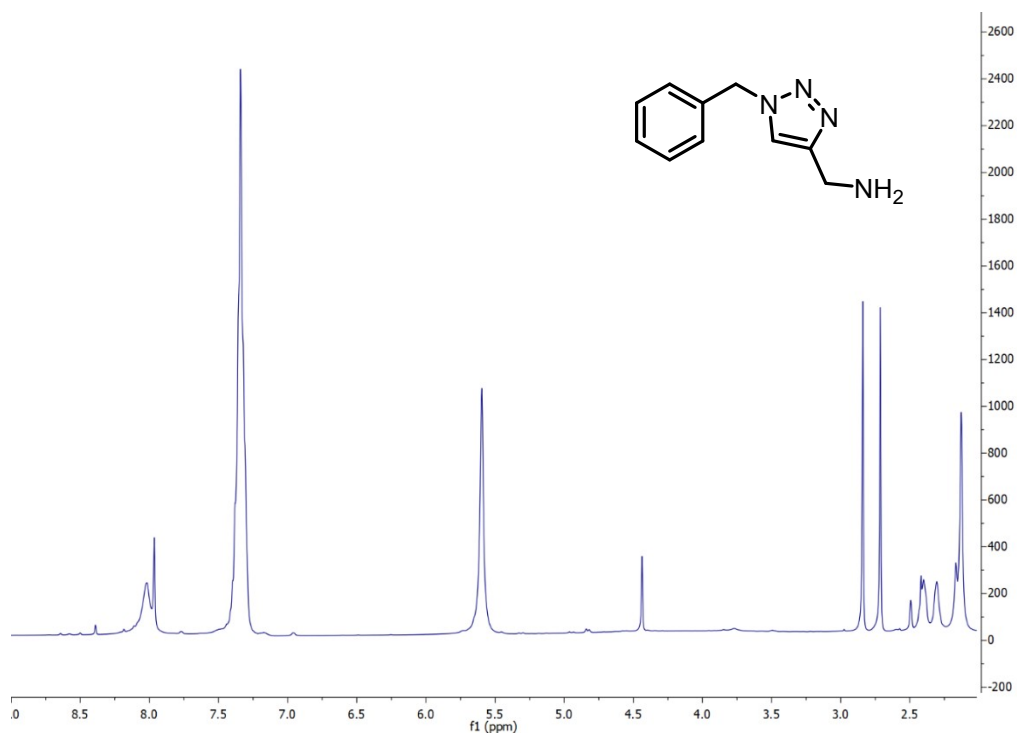
Block copolymerization of polystyrene with poly( $\epsilon$ -caprolactone) took place via the standard Schlenk technique with a glass vacuum manifold connected to an inlet of nitrogen. PCL was dissolved in 2 mL DMF and then  $\text{CuCl}_2/\text{PMDETA}$  (1 eq.) complex was added to the solution. After 5 min.,  $\omega$ -azido terminated polystyrene was added to the above-mentioned solution. The Schlenk tube was degassed using three freeze-pump-thaw cycles prior to lightening. After the given time, the copper complex was removed from the solution via a basic alumina column and the solution was concentrated. The concentrated solution was precipitated into excess methanol then the polymer was collected and dried under a high-pressure vacuum overnight.

### **Photoinduced Crosslinked Polymer Formation**

Az-1 and Alk-1 were mixed in an equal ratio (1 eq.) with  $\text{CuCl}_2$  (0.05 eq.) and PMDETA (0.1eq.) in a small transparent vial and 10 mg mpg-CN was added to the vial. The solution was mixed until homogeneous and then UCG was placed in a vial. After gelation was completed after 2 hours. Subsequently, the gel was placed in DCM for 24h hours, then filtered. The final product was dried for 24h in a vacuum oven.



**Figure S8.** <sup>1</sup>H-NMR spectrum of (1-benzyl-1H-1,2,3-triazol-4-yl)methanol.



**Figure S9.** <sup>1</sup>H-NMR spectrum of (1-benzyl-1H-1,2,3-triazol-4-yl)methanamine

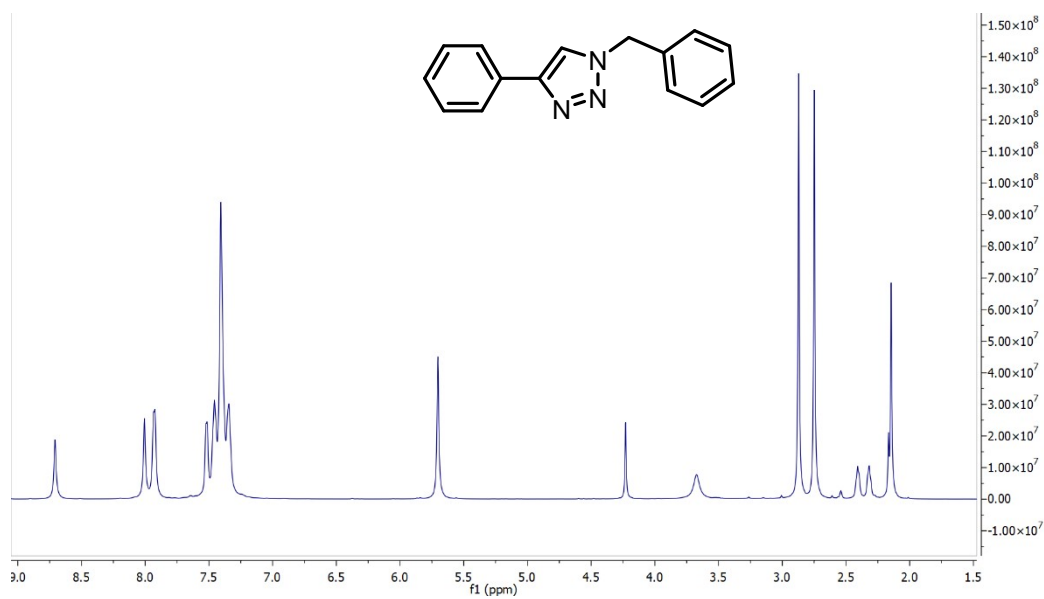


Figure S10. <sup>1</sup>H-NMR spectrum of 4-benzyl-1-phenyl-1H-1,2,3-triazole

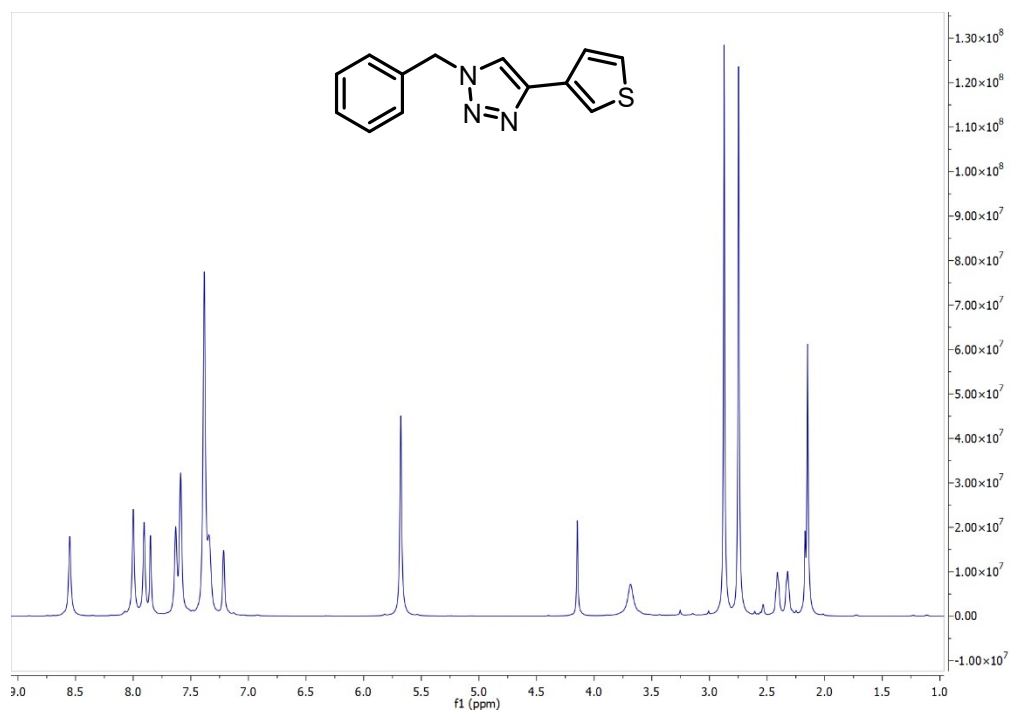
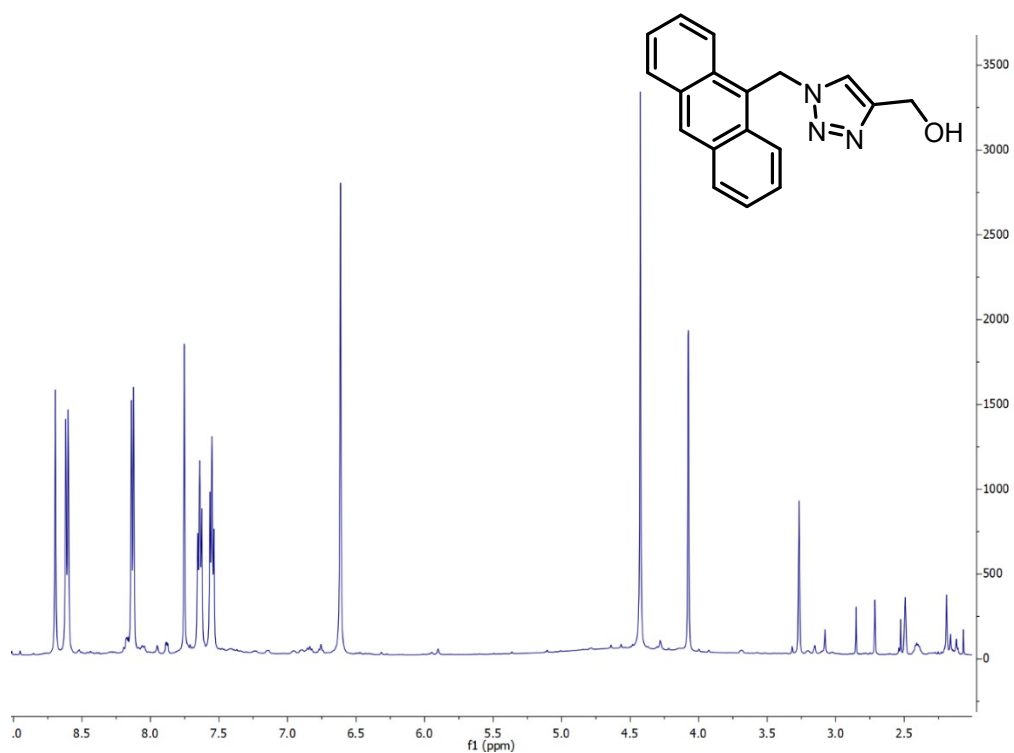
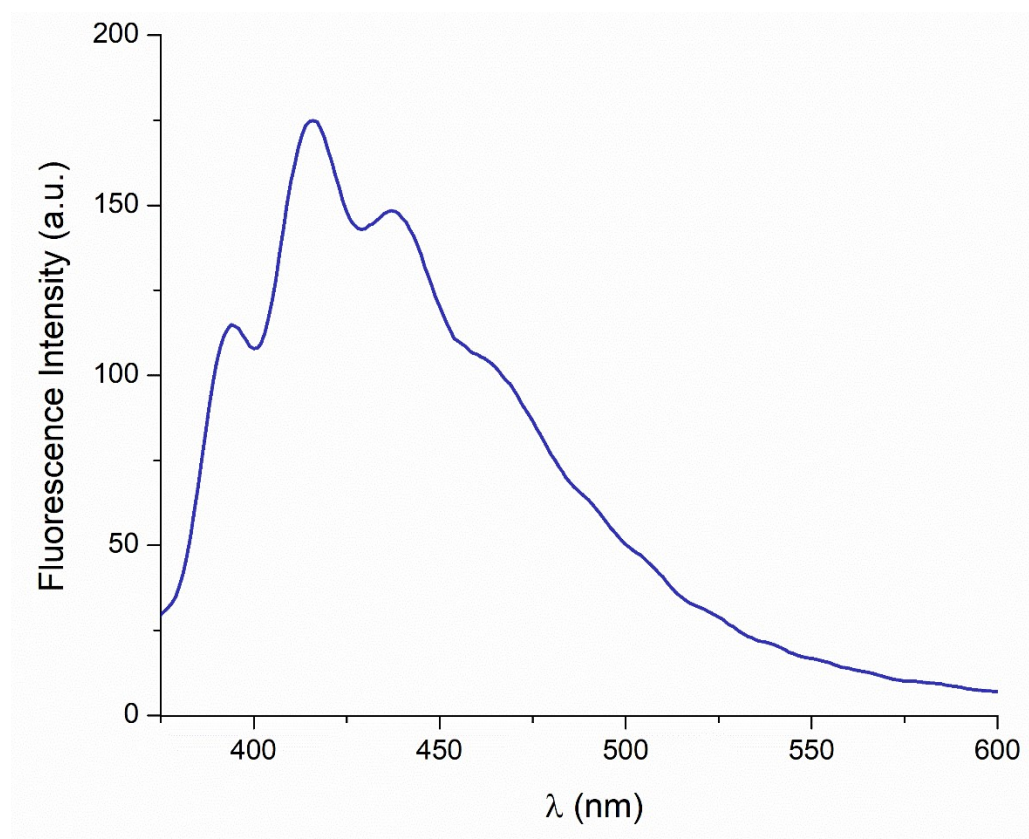


Figure S11. <sup>1</sup>H-NMR spectrum of 1-benzyl-4-(thiophen-3-yl)-1H-1,2,3-triazole

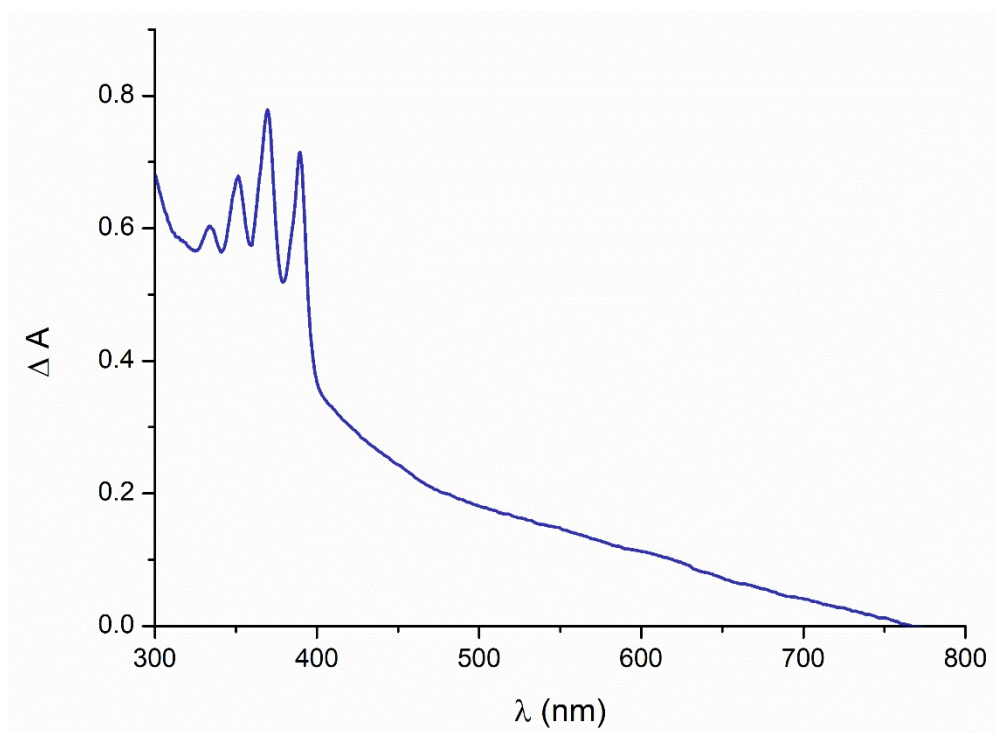


**Figure S12.** <sup>1</sup>H-NMR spectrum of (1-(anthracen-9-ylmethyl)-1H-1,2,3-triazol-4-yl)methanol

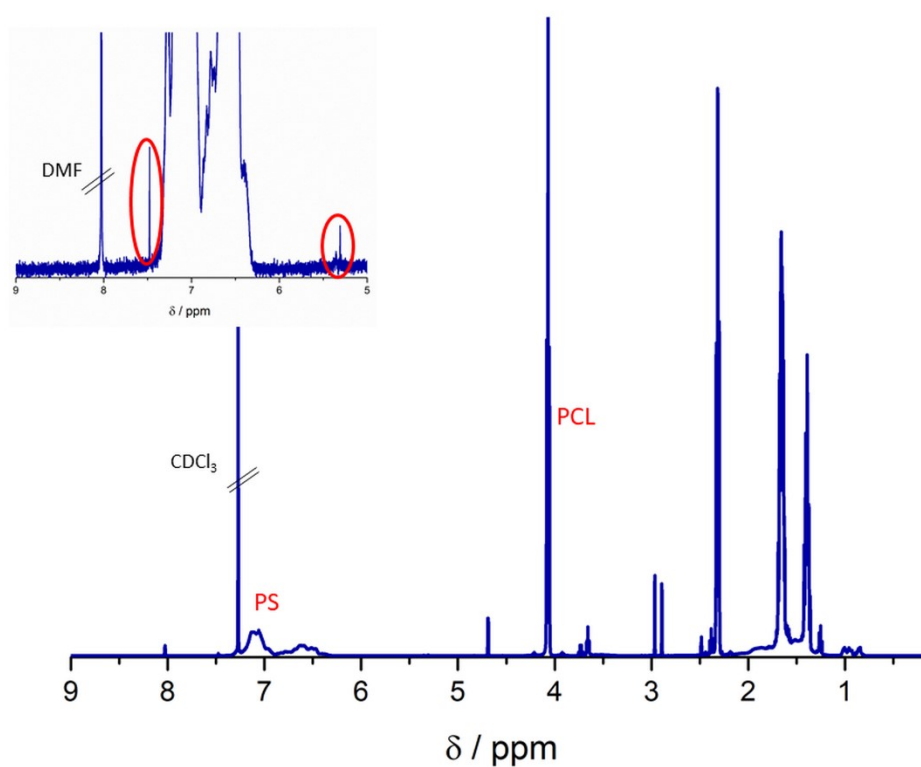


**Figure S13.** Fluorescence spectrum of anthracene functional poly(ε-caprolactone).





**Figure S14.** UV-Vis spectrum of anthracene functional poly( $\epsilon$ -caprolactone).



**Figure S15.**  $^1\text{H}$  NMR spectrum of the block copolymer.

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