

A Catalytic System Based on π - π Stacking Interactions Between Pyrene Substituted Gold NHC Catalyst and Amphiphilic Polymers for Alkyne Hydration Reactions

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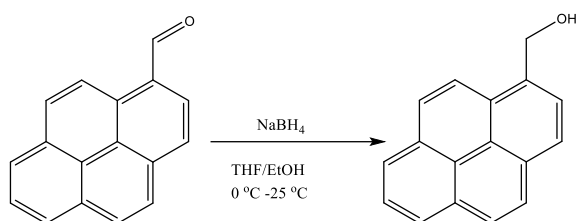
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Experimental Section

Otherwise noted all chemicals are purchased from Sigma-Aldrich and used as received. CH₂Cl₂ was dried and distilled over P₂O₅ and stored under a nitrogen atmosphere. ¹H and ¹³C NMR spectra were recorded at 25 °C with a Bruker GmbH 400 MHz high-performance digital FT-NMR spectrometer using CDCl₃ and d₆-DMSO as the NMR solvents.

GC-MS analyses were performed using Shimadzu GC-MS QP2010-Plus equipped with Restek Rxi-5Sil column (30m x 0.25 mm x 0.25 μm) with a constant helium flow rate of 1 ml/min. vent. The analysis was performed on the following column system operating on THF (flow rate 1 mL/min) at 40 °C. The main-column PSS SDV analytical (5 μm, 300 mm × 8.0 mm, 10,000 Å) and a PSS SDV analytical pre-column (5 μm, 50 mm × 8.0 mm). The calibration was created using narrow linear poly(methylmethacrylate) standards (Polymer Standards Service PPS, Germany) ranging from 1100 to 981,000 Da. Dynamic light scattering (DLS) analysis was carried out using a Malvern Seta-Sizer Nano-ZS90 with a fixed scattering angle 90°. High contrast transmission electron microscopy (TEM) images were recorded at METU Central Lab (Ankara) with an FEI Tecnai G2 Spirit Bio(TWIN) TEM at 120 kV using carbon-filmed coated copper grids.

Synthesis of 1-Pyrenemethanol



Scheme S1. Synthesis of 1-pyrenemethanol

1-pyrenecarboxaldehyde (1.0 g, 4.34 mmol) was dissolved in 50 mL dry THF in 100 mL glass flask and magnetically stirred for 30 minutes under nitrogen atmosphere (Scheme S1). In a separate flask, NaBH₄ (0.49 g, 13.0 mmol) and NaOH (34.0 mg, 0.86 mmol) in ethanol (25 mL) were dispersed under an ice bath. The flask bearing 1-pyrenecarboxaldehyde was taken to an ice bath and NaBH₄ solution was added dropwise under a nitrogen atmosphere and stirred for one hour and then the reaction vessel was taken to room temperature and stirred for 24 h. After that, the reaction mixture was neutralized by washing with 0.1 M HCl solution. Then the reaction mixture was extracted with saturated K₂CO₃ solution (10 mL x 2) and then the organic phase was dried over MgSO₄ and filtrated. The solvent was evaporated under a high vacuum, yielding a white solid with 80 % yield. The resulting product was characterized by ¹H NMR and MS (EI) spectroscopy (Figure S1 and Figure S2).

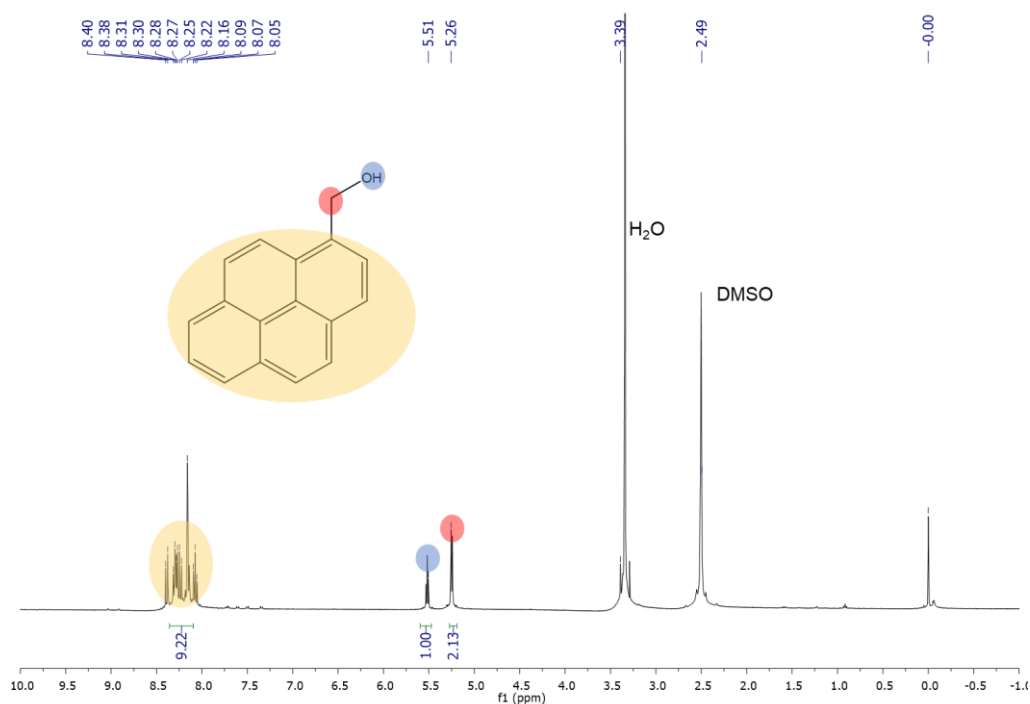


Figure S1. ¹H NMR spectrum of 1-pyrene methanol (400 MHz, d₆-DMSO)

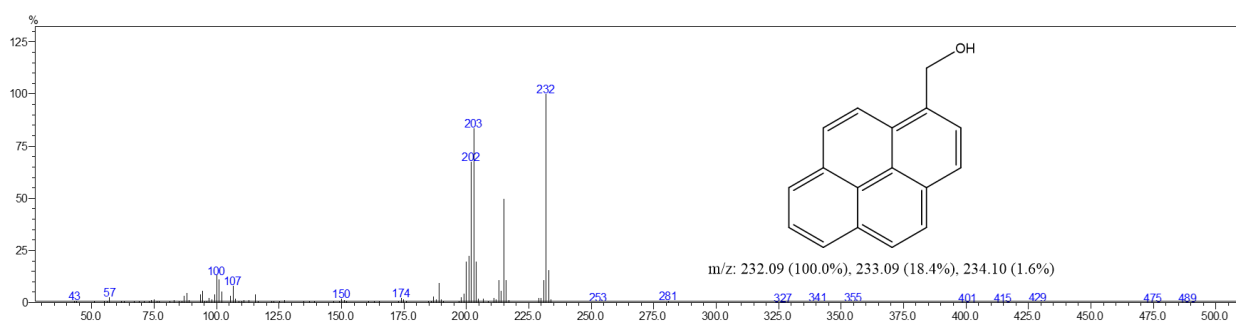
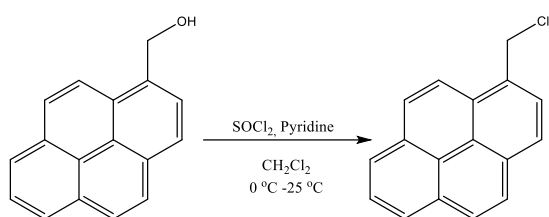


Figure S2. MS (EI) spectrum of 1-pyrene methanol

Synthesis of 1-Chloromethylpyrene



Scheme S2. Synthesis of 1-chloromethyl pyrene

1-pyrenemethanol (6.0 mmol, 1.39 g) was dissolved in 50 mL of dry dichloromethane in a two-necked 100 mL glass vessel. Thionyl chloride (6.1 mmol, 0.725 g) was added to the reaction media under a nitrogen atmosphere and stirred for five minutes (Scheme S2). Pyridine (6.1 mmol, 0.482 g) was added dropwise to the reaction medium. Following the addition of pyridine, the reaction mixture was magnetically stirred at room temperature overnight. The reaction mixture extracted with deionized water (20 mL x 2) and the organic phase was dried over MgSO₄. The organic solvent was evaporated by vacuum. The resulting dark yellow solid obtained in 80 % yield. The resulting product was characterized by ¹H NMR and MS (EI) spectroscopy (Figure S3 and S4).

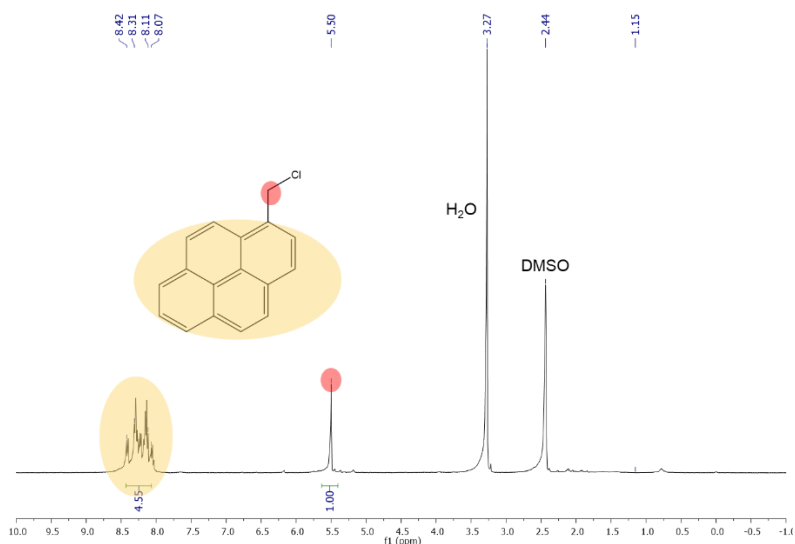


Figure S3. ^1H NMR spectrum of 1-chloromethylpyrene (400 MHz, d_6 -DMSO)

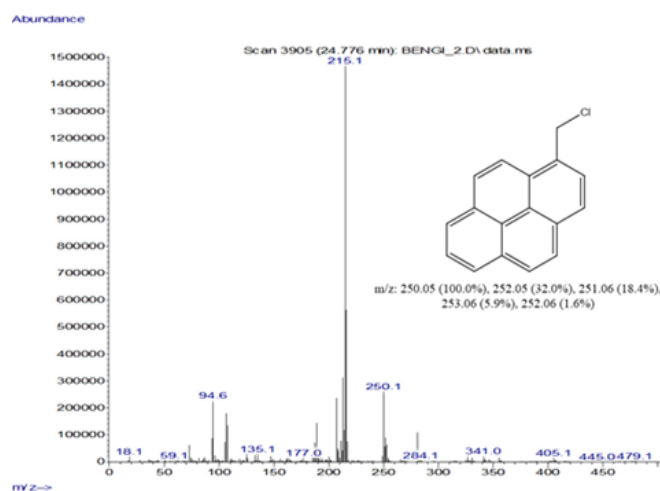
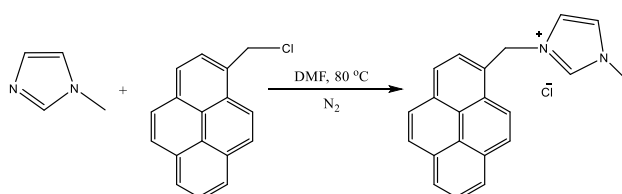


Figure S4. MS(EI) spectrum of 1-chloromethyl pyrene

Synthesis of L1



Scheme S3. Synthesis of L1

1-methylimidazole (0.22 g, 2.70 mmol) and 1-chloromethyl pyrene (0.61 g, 2.44 mmol) was taken to a 100 mL round bottom glass flask (Scheme S3). Dry DMF (5 mL) was added to the reaction flask and stirred at 80 °C under nitrogen atmosphere for 24 h. After 24 h, the reaction mixture was cooled down to room temperature, DMF was removed under high vacuum. The resulting white solid was washed with ethanol and dried under vacuum at 25 °C (Yield: 72 %).

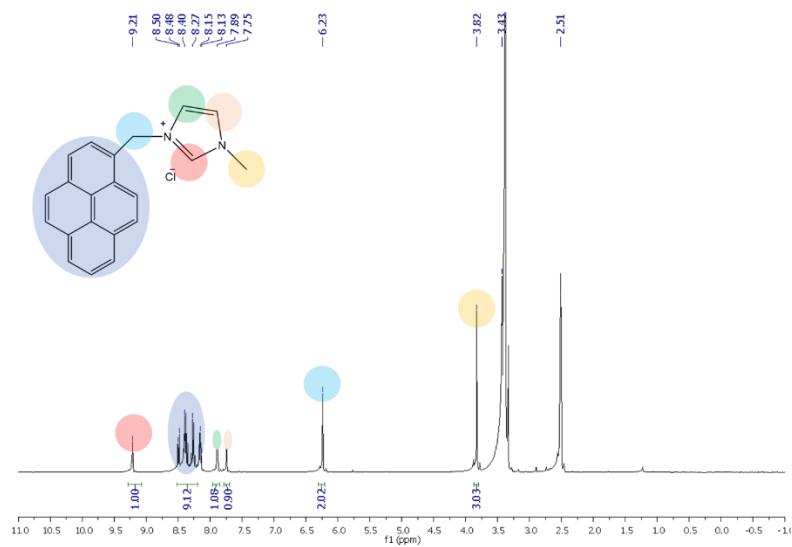


Figure S5. ^1H NMR spectrum of L1 (400 MHz, d_6 -DMSO)

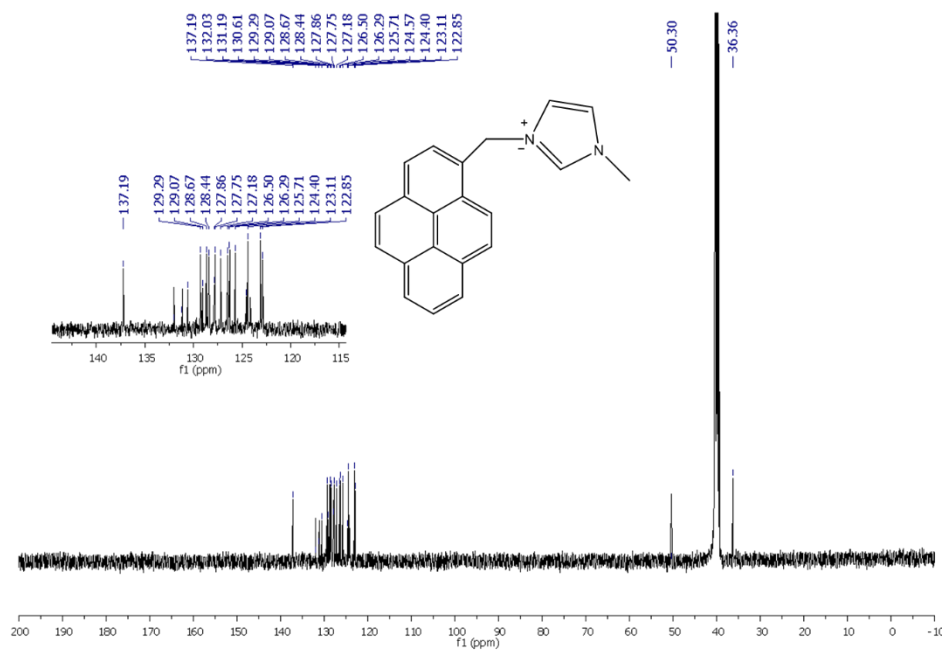


Figure S6. ^{13}C NMR spectrum of L1 (100 MHz, d_6 -DMSO)

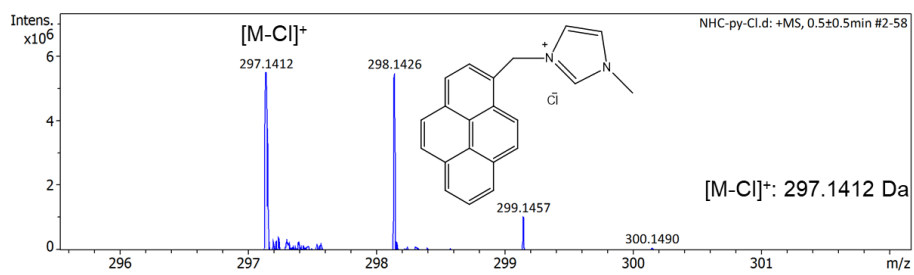
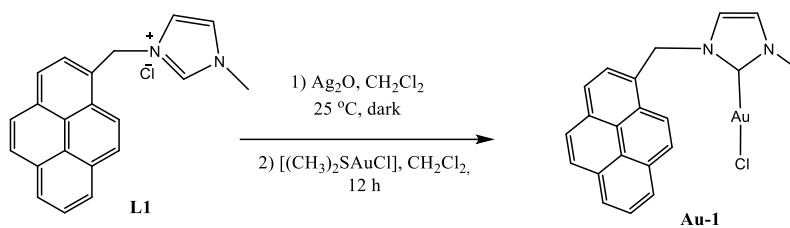


Figure S7. ESI-MS spectrum of L1

Synthesis of Au-1



Scheme S4. Synthesis of Au-1

Au-1 complex was synthesized following the literature protocol [1]. A Schlenk reactor was charged with L1 (0.10 g, 0.30 mmol) and dry dichloromethane (5.0 mL). Ag_2O (0.037 g, 0.16 mmol) was added to the reaction media under a nitrogen atmosphere and the reaction mixture was stirred at room temperature in a dark environment (Scheme S4). After 24 h, reaction mixture was filtered through a short pad of silica gel (1 cm) and the column was washed with additional 5 mL of dichloromethane. The filtrate was taken to another Schlenk flask and chloro(dimethylsulfide)gold (I) (88 mg, 0.30 mmol) was added to the reaction mixture and stirred at 12 h under nitrogen atmosphere. After that, the solvent was removed by vacuum and the resulting solid was washed with n-pentane (-24 °C). A white solid was isolated in 60 % yield. Au-1 was characterized by ^1H NMR, ^{13}C NMR and ESI-MS.

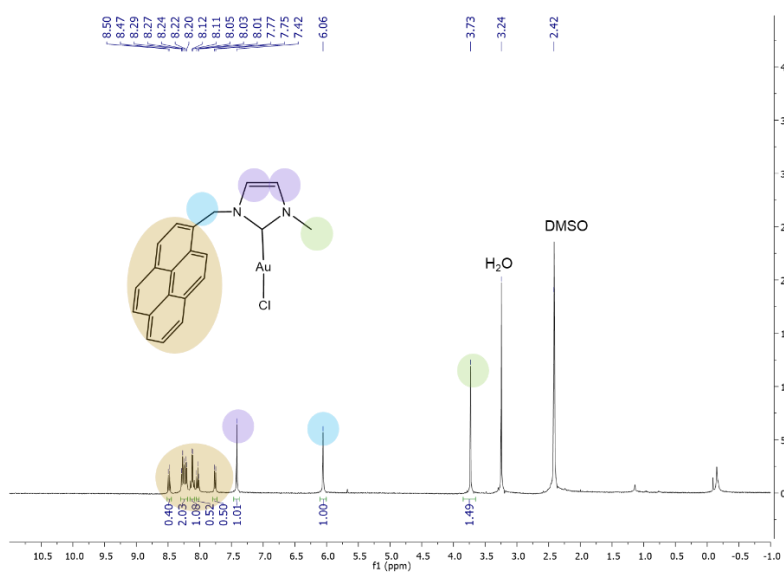
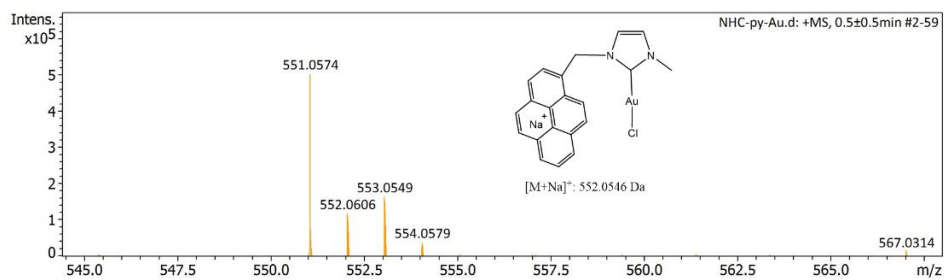
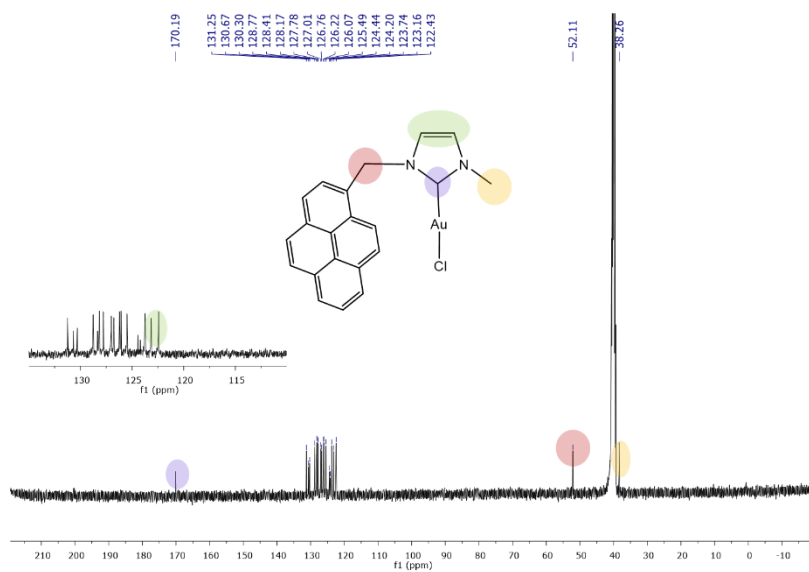
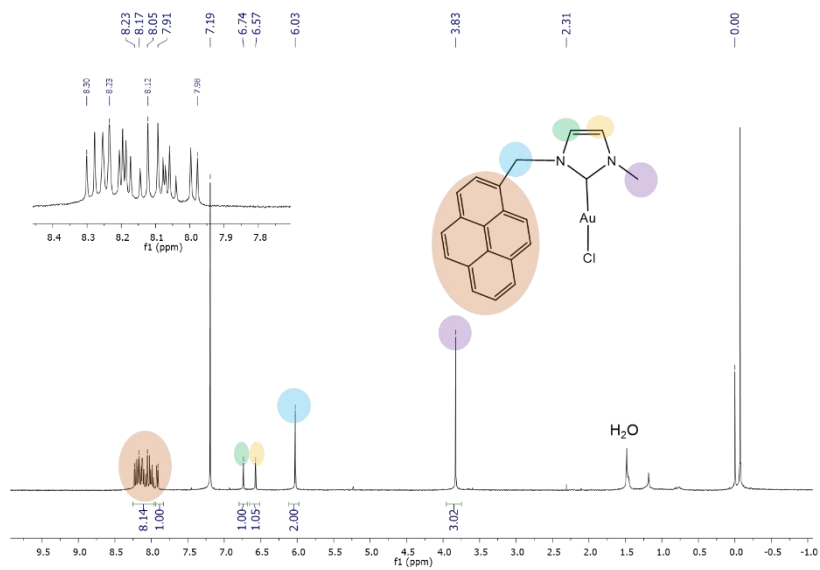
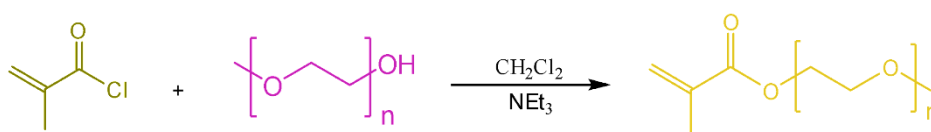


Figure S8. ^1H NMR spectrum of Au-1 (400 MHz, d_6 -DMSO)



Synthesis of Hydrophilic Monomer (M2)

A three-necked glass flask (250 mL) was charged with polyethylene glycol methyl ether (M_n : 2000 Da, 10 g) and dry dichloromethane (20 mL) under a nitrogen atmosphere. The reaction mixture was cooled down to 0-4 °C and triethylamine (3.0 mol equivalent, 2.1 mL) was introduced into the reaction vessel. After five minutes of intense stirring under ice bath, methacryloyl chloride (2.2 mol equivalent, 1.15 g, 1.10 mL) was added dropwise to the reaction media. Once the addition completed, the reaction mixture was stirred overnight. After that, the reaction mixture was filtrated and poured into cold diethyl ether to precipitate the product. A white milky solid was isolated in the first batch. The resulting solid was purified by redissolved in dichloromethane and precipitation in diethyl ether. The resulting product was characterized by ^1H NMR and MALDI-ToF MS.



Scheme S5. Synthesis of M2

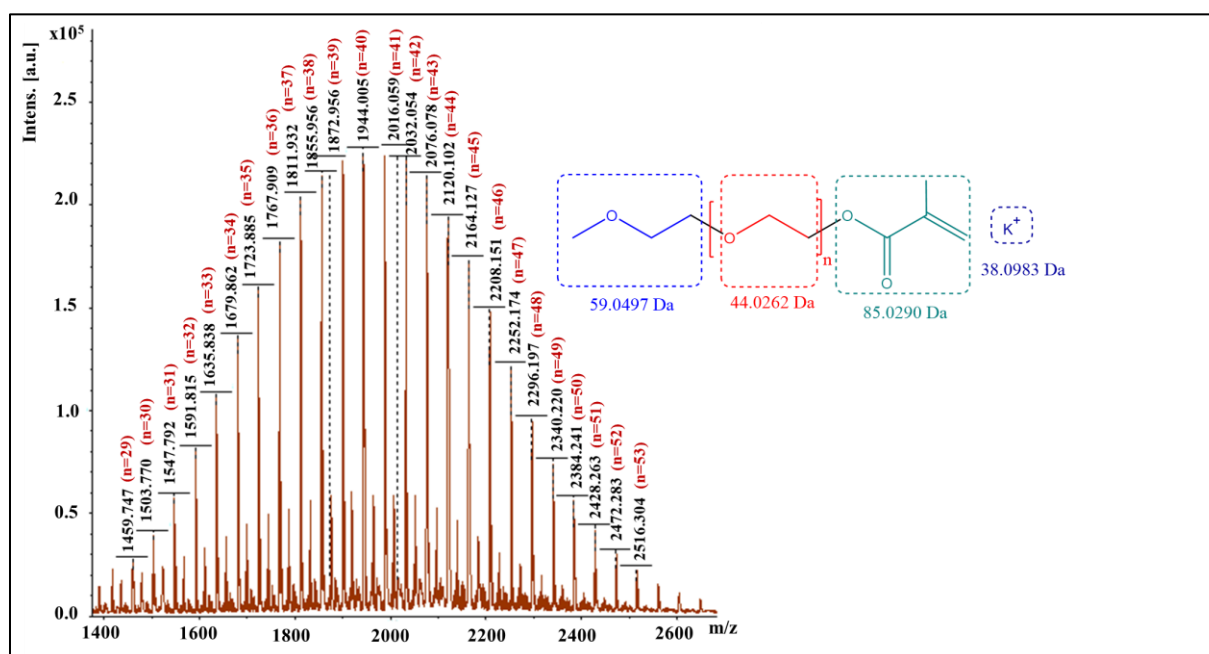


Figure S12. MALDI ToF-MS spectrum of M2

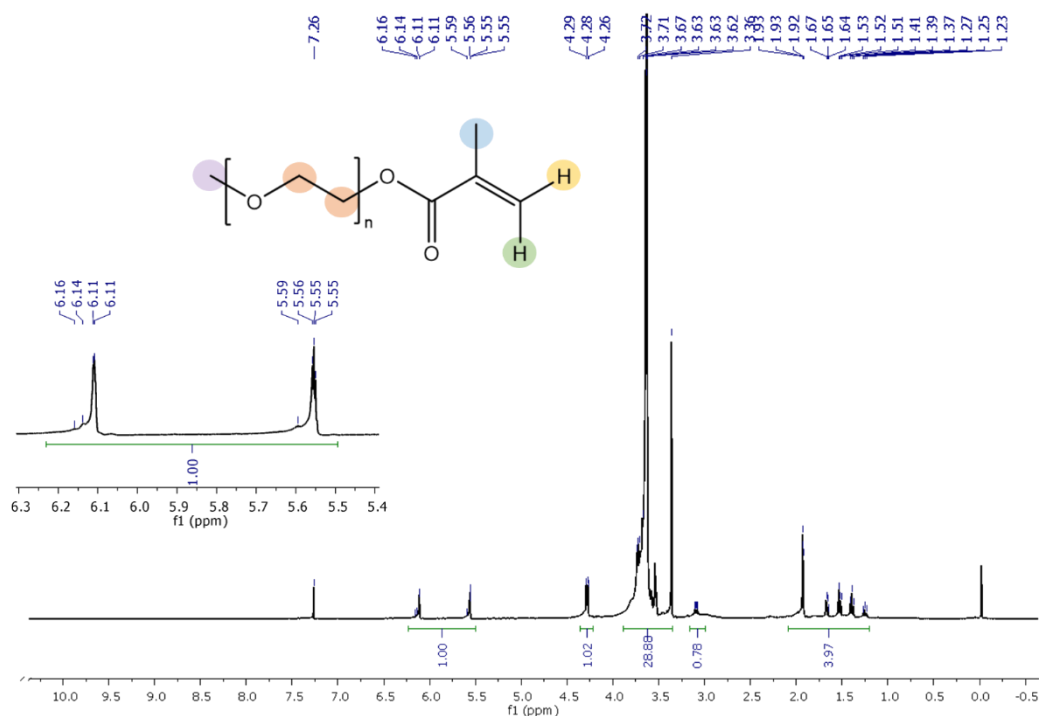
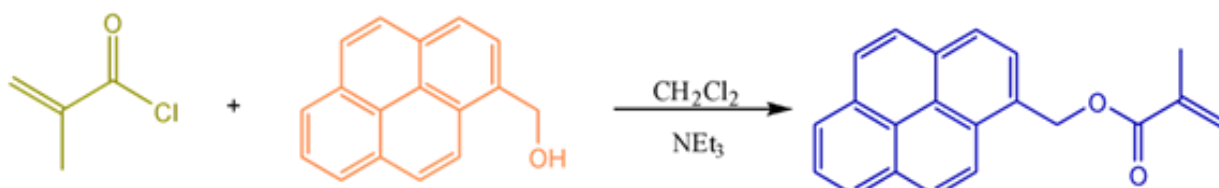


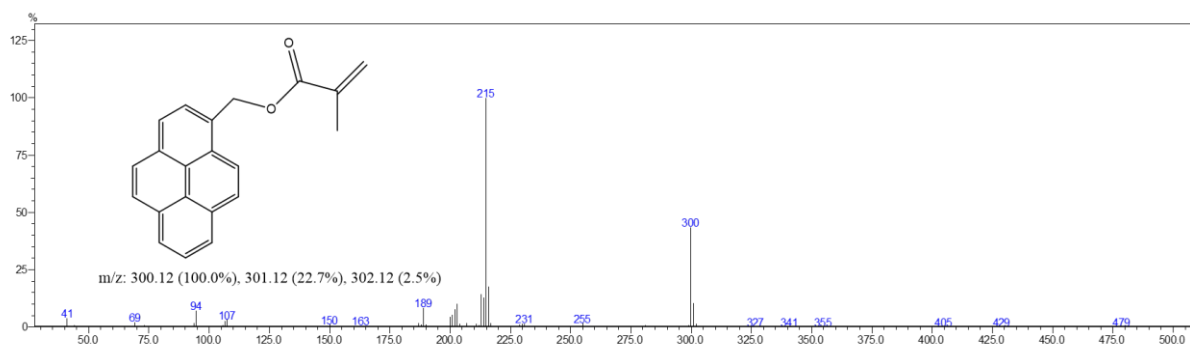
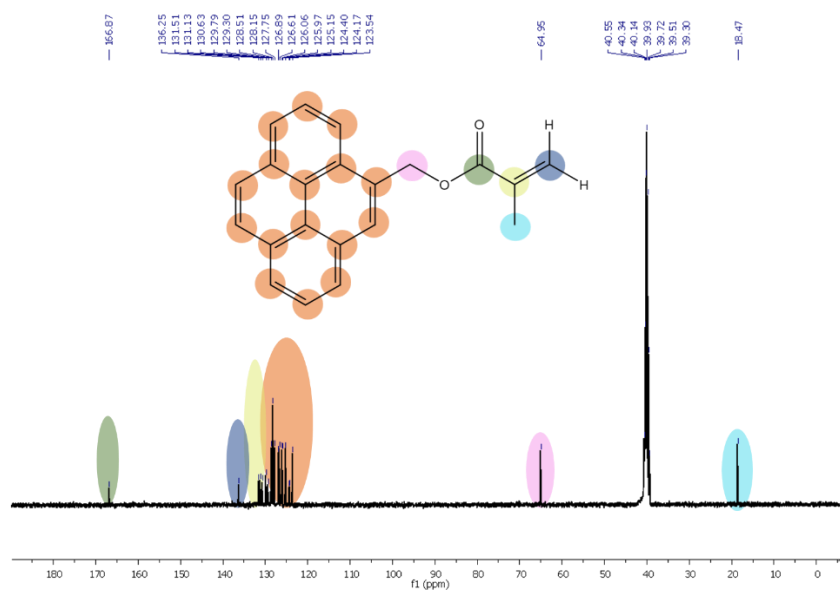
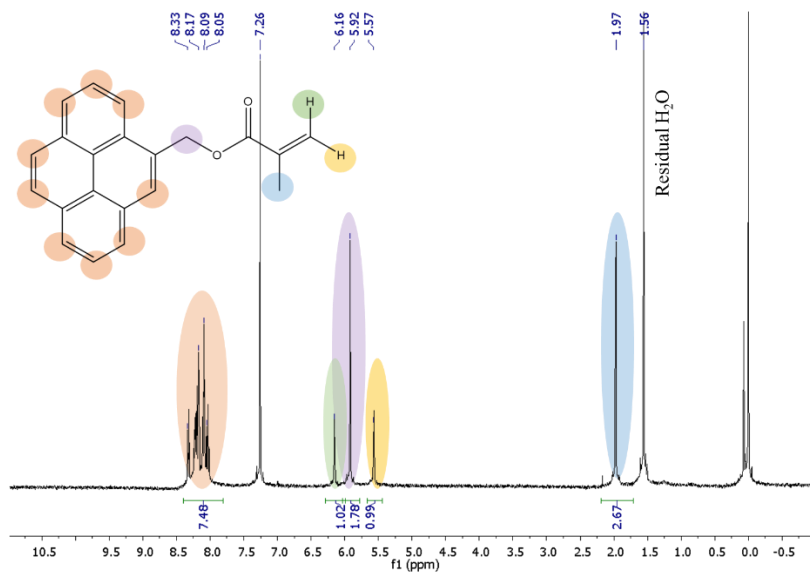
Figure S13. ^1H NMR spectrum of M2 (400 MHz, CDCl_3)

Synthesis of Hydrophobic Monomer (M1)

A three-necked glass flask (250 mL) was charged with 1-pyrene methanol (1.0 mol equivalent, 1.0 g, 4.31 mmol) and dry dichloromethane (15 mL) under a nitrogen atmosphere. The reaction mixture was cooled down to 0-4 °C and triethylamine (2.5 mol equivalent, 1.75 mL) was introduced into the reaction vessel. After five minutes of intense stirring under ice bath, methacryloyl chloride (2.5 mol equivalent, 1.30 g, 1.24 mL) was added dropwise to the reaction media. Once the addition was completed, the reaction mixture was stirred overnight. After that, the reaction mixture was filtrated and washed with saturated NaCl solution (15 mL x 2). The organic layer was then washed again with deionized water (15 mL x 2). The organic phase was dried over MgSO_4 and the solvent was removed under vacuum. The resulting yellowish solid was recrystallized in ethanol, yielding an off-white solid in 65 % yield. The resulting product was characterized by ^1H NMR and MS (EI) spectroscopy.

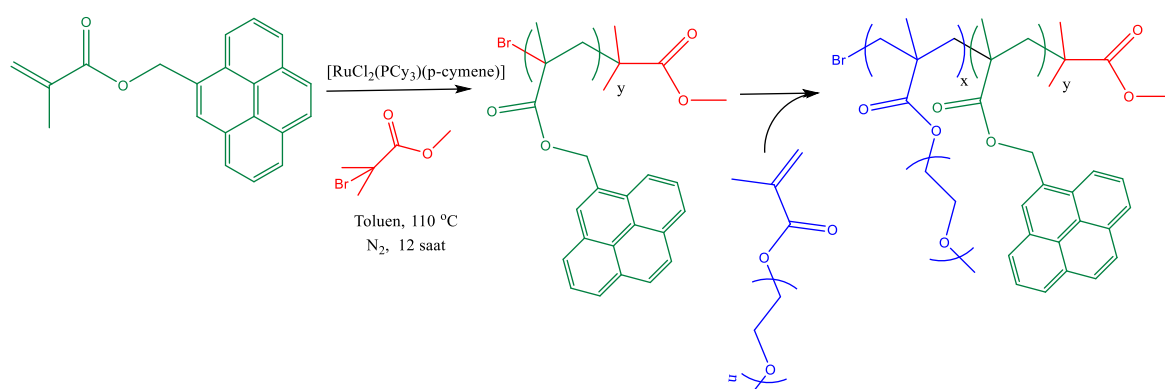


Scheme S6. Synthesis of M1



Synthesis of ATRP Polymers

A Schlenk reactor was charged with hydrophobic monomer (M1) (2.0 g, 6.7 mmol) dissolved in 2 mL of dry toluene at room temperature. The ATRP initiator; methyl- α -bromoisobutyrate (0.067 mmol, 0.012 g) was added to the reaction media and nitrogen gas was purged for 10 minutes. Then $[\text{RuCl}_2(\text{PCy}_3)(\text{p-cymene})]$ (4.0 mg, 0.067 mmol) was added to the reaction media to initiate the ATRP reactions at 110 °C (Scheme S7). Following the complete consumption of M1, hydrophilic monomer (M2, 0.67 mmol, 1.34 g) was added to the reaction media and stirred at 110 °C for 12 h. The reaction was quenched by opening the cap of the reactor to the open air. The reaction mixture was poured into cold diethyl ether. The polymer mixture was dissolved in a water/methanol mixture to separate the homopolymer of M1 which is insoluble in the aqueous phase. After filtration and evaporation of the solvent, the resulting light brown-colored polymer was characterized using ^1H , ^{13}C NMR, and size exclusion chromatography (SEC).



Scheme S7. Synthesis of amphiphilic ATRP polymers (P1)

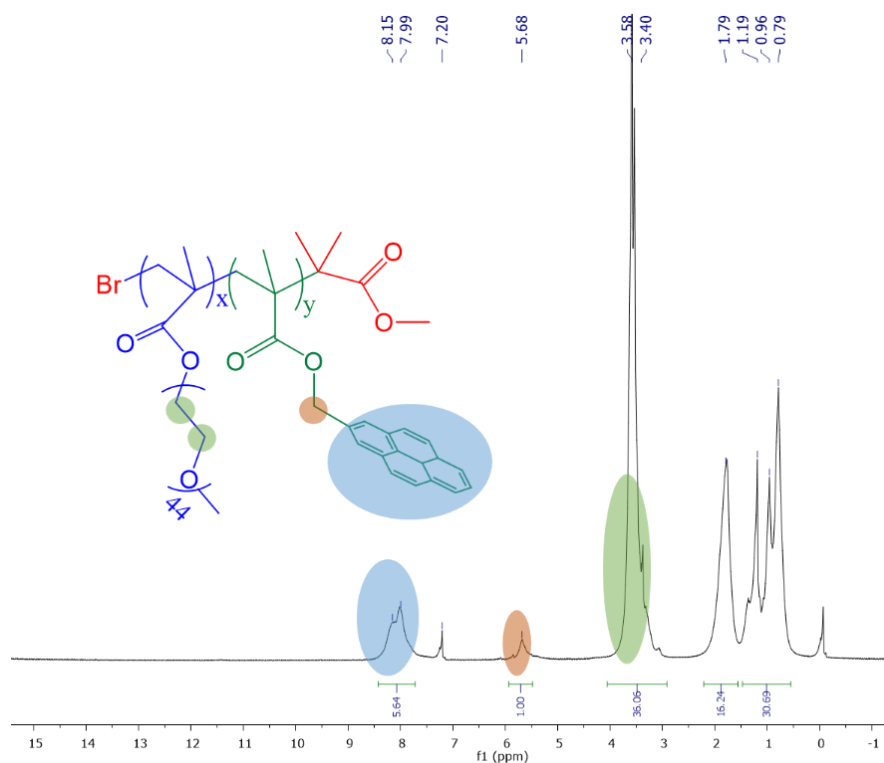


Figure S17. ^1H NMR spectrum of P1 (400 MHz, CDCl_3)

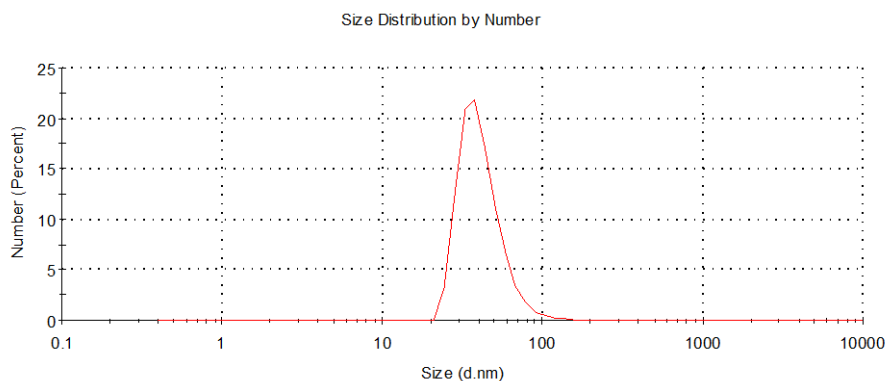


Figure S18. Dynamic light scattering (DLS) of P1 in MeOH/H₂O

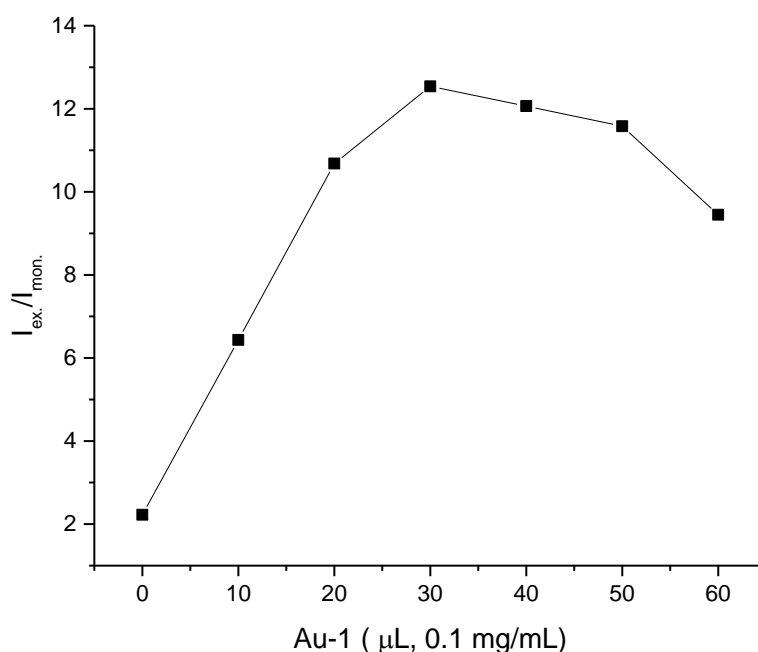


Figure S19. $I_{ex}/I_{mon.}$ fluorescence emission signal intensity

Representative Procedure for Au-1@P1 Catalyzed Alkyne Hydration Reactions and Reusability Experiments

A Schlenk reactor was charged with Au-1 (5 mg, 0.0095 mmol) and P1 (0.20 g) and MeOH/H₂O mixture (v/v: 1/1, 2 mL). The reaction mixture was sonicated for five minutes and then the reactor was equipped with a magnetic stirrer. Phenylacetylene (0.95 mmol, 104 μL) was added to the reactor and stirred for five minutes and then H₂SO₄ (4.75 M, 10 μL) was added to the reaction media to initiate the reaction. The reaction mixture was taken to a pre-heated oil bath at 80 °C. Aliquots (10 μL) were taken from the reaction mixture at regular intervals and diluted with 10 mL of methanol and analyzed by GC-MS. Once the conversion of phenylacetylene reached a plateau, the reaction mixture was cooled down to room temperature and then the organic phase was extracted with diethyl ether.

For reusability experiments, the micellar catalyst which stayed in the aqueous phase was taken to a new reactor and diluted with 1 mL methanol, and stirred for five minutes. After that phenylacetylene (0.95 mmol, 104 μ L) was added to the reactor and stirred for five minutes and then H₂SO₄ (4.75 M, 10 μ L) was added to the reaction media to initiate the reaction.

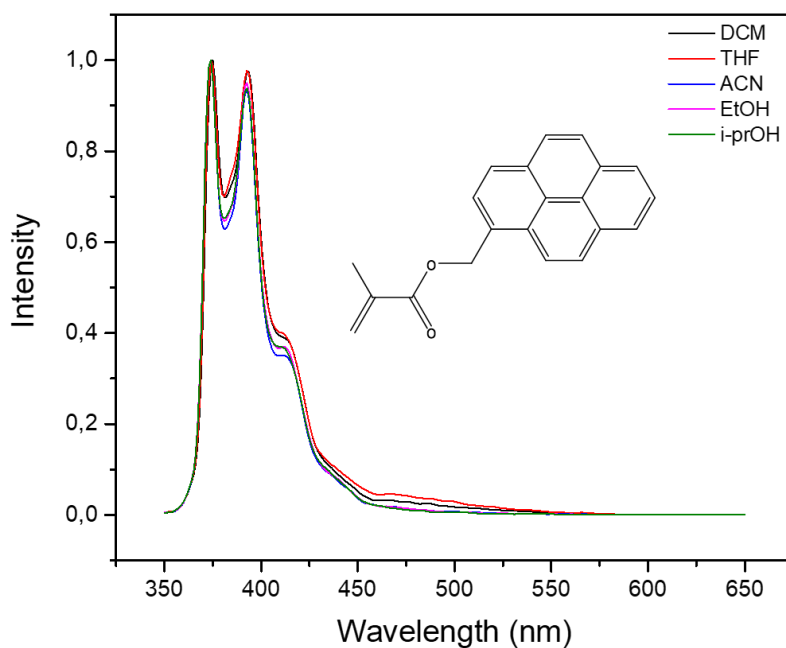


Figure S20. Fluorescence spectrum of hydrophobic monomer in different solvents

Table S1. Hydration of phenylacetylene in different binary solvent mixtures

Solvent (v/v; 1/1)	% Au-1 (mol %)	Additive (5 mol %)	Time (h)	Conversion %	Yield %
MeOH/H ₂ O	1	H ₂ SO ₄	18	99	95
THF/H ₂ O	1	H ₂ SO ₄	24	75	70
1,4-dioxane/H ₂ O	1	H ₂ SO ₄	24	58	55

REFERENCES

[1] D. Ventura-Espinosa, S. Sabater, J. A. Mata, *J. Catal.*, 2017, 352, 498