Supporting Information
for
Luminescent Hyperbranched Polymers: Combining Thiol-Yne Chemistry with Gold-mediated C-H Bond Activation

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**Experimental:** All reagents were used as obtained unless otherwise stated. Prop-2-yl-1-ol and 2,2-dimethoxy-2-phenyl-acetophenone (DMPA) were purchased from Aldrich. 3-mercaptopropionic acid was purchased from Merck. Sulfuric acid and triethylamine and high purity dichloromethane (DCM) were purchased from Ajax chemicals. N,N-dimethyl formamide (DMF) was purchased from Fluka. The [Au(Im)(OH)] was prepared according to the literature procedure.

**Nuclear Magnetic Resonance (NMR):** NMR analysis of the PYMP and poly(PYMP) material was performed on a Bruker AVANCE200 NMR Spectrometer, with an Oxford narrow bore magnet and 5mm dual(CH) probes with z-gradients. NMR analysis was performed on the XWINNMR3.5 and iNMR 0.7 software.

**Multiple Detection Size Exclusion Chromatography (SEC):** Molecular weights were determined using a Polymer Laboratories GPC-50-Plus SEC system with a Polymer Laboratories PG-Gel 5µM guard column and two Polymer Laboratories Mixed-C columns. The system was equipped with a PL-RI Differential Refractive Index detector (DRI), PL-BV 400RT Viscometer (Visc). The eluent was THF at a flow rate of 1 mL/min. The system was calibrated using Polystyrene standards with molecular weights in the range of 915000-168 g/mol. All analysis was performed using the Cirrus Software, employing Universal Calibration (UC).

**Infrared Spectroscopy:** IR spectra were recorded on Bruker Spectrum GX FTIR system. Samples were prepared as KBr pellets.

**Absorption, Emission and Excitation Spectroscopy:** Emission and excitation spectra were obtained using a Varian Cary Eclipse fluorescence spectrophotometer. The instrument was controlled using the Cary Eclipse Scan application. Absorbance spectra for the quantum yield calculations were determined using a Varian Cary 4E UV-Visible spectrophotometer, and luminescence spectra for the quantum yield determination were obtained using a Perkin Elmer LS 50 B luminescence spectrometer.

**Luminescence Lifetime Determination:** The luminescence lifetime was obtained using a TOPAS tunable laser pumped by a femtosecond Clark MXR CPA 2210 laser operating
at 1kHz to obtain 350nm excitation. The delayed luminescence was recorded by an iCCD camera attached on a spectrapro 2300i monochromator (Princeton Instruments).

**Synthesis of prop-2-ynyl 3-mercaptopropanoate (PYMP):**

![Chemical structure](image)

**Scheme S1.** Synthesis of PYMP, a small molecule bearing a thiol and alkyne.

Prop-2-yn-1-ol (Aldrich, 7.16g, 127.4 mmol) was added to 3-mercaptopropionic acid (2.75g, 25.9 mmol). To this solution sulphuric acid (0.76g 7.8 mmol) was added and the solution was heated at 85 °C for 2 hours. The solution was cooled to room temperature and left to sit for 0.5 hour. The reaction mixture was dissolved in 60 mL of dichloromethane, and triethylamine (3.0 g, 29.7 mmol) was added to this solution. This mixture was washed four times with 50 mL of water. The crude product was purified by silica gel chromatography using an eluent of 80% hexane and 20% ethyl acetate. The final impurities were removed by passing the product over a short silica column using 100% toluene as an eluent, and excess toluene removed under reduced pressure. This reaction is shown in Scheme S1. This yielded PYMP, with residual toluene (1.99g). The purity of the product (PYMP) was confirmed using proton NMR, $^1$H-NMR(200 MHz, CDCl$_3$) δ ppm 2.48 (1H, t, $J = 4.95$ Hz, H-C≡C) 4.71 (2H, d, $J = 2.48$ Hz, C≡C-C$_2$H$_2$-O), 1.65 (1H, t, $J = 8.31$ Hz, SH) and 2.74 (4H, m, C(O)-CH$_2$-CH$_2$-S). The only impurity present was toluene, with molar ratio PYMP:Toluene = 1:1.6.

**PhotoPolymerization of PYMP:** PYMP, toluene, DMF and DMPA were combined together as described in Table S1 to make 5 batch solution. Each batch solution was divided into 2 glass vials, and each vial was capped with a rubber septum, and wrapped in aluminium foil and degassed by bubbling nitrogen for 2 min. The Vials were placed under a UV lamp for 1 hour. All reactions were performed in a dark box illuminated by a Spectroline ENF-280C/FE lamp irradiating at 365 nm. After the reaction time, each vial was exposed to air, and wrapped in aluminium foil. Each sample was analysed by SEC.
Conversion was determined by integrating both the unreacted and reacted propargyl ester region in the NMR (4.2-4.8 ppm) and comparing this to the integral of the unreacted propargyl ester (4.7-4.8 ppm). The conversion was determined using the following formula:

\[
\text{Conversion} = 2 \times \frac{I_A - I_U}{I_A},
\]

where \( I_A \) is the integral under both the reacted and unreacted propargyl esters, while \( I_U \) is the integral under just the unreacted ester. Each sample was found to reach very high conversion polymer, and the SEC traces showed the presence of high molecular weight species in all samples.

<table>
<thead>
<tr>
<th></th>
<th>PYMP</th>
<th>Toluene</th>
<th>DMF</th>
<th>DMPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass Batch 1 (g)</td>
<td>0.1286</td>
<td>0.1659</td>
<td>0.4466</td>
<td>0.006</td>
</tr>
<tr>
<td>Moles Batch 1 (mmol)</td>
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<td>1.803</td>
<td>6.114</td>
<td>0.023</td>
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<tr>
<td>Mass Batch 2 (g)</td>
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<td>0.1748</td>
<td>0.4407</td>
<td>0.0061</td>
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<tr>
<td>Moles Batch 2 (mmol)</td>
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<td>6.033</td>
<td>0.024</td>
</tr>
<tr>
<td>Mass Batch 3 (g)</td>
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<td>0.1753</td>
<td>0.4514</td>
<td>0.0060</td>
</tr>
<tr>
<td>Moles Batch 3 (mmol)</td>
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<td>1.904</td>
<td>6.179</td>
<td>0.023</td>
</tr>
<tr>
<td>Mass Batch 4 (g)</td>
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<td>Moles Batch 4 (mmol)</td>
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<td>6.089</td>
<td>0.023</td>
</tr>
<tr>
<td>Mass Batch 5 (g)</td>
<td>0.1596</td>
<td>0.2058</td>
<td>0.6815</td>
<td>0.0094</td>
</tr>
<tr>
<td>Moles Batch 5 (mmol)</td>
<td>1.398</td>
<td>2.236</td>
<td>9.329</td>
<td>0.037</td>
</tr>
</tbody>
</table>

**Purification of poly(PYMP):** The five samples of poly(PYMP) in DMF were combined, and precipitated into twice methanol. The suspension was centrifuged and the sediment collected as a viscous liquid. The supernatant fractions were collected and the methanol removed under reduced pressure. The residual poly(PYMP) and DMF were precipitated from hexane to remove excess DMPA. The polymer and DMF were dissolved in dichloromethane (50 mL) and washed with water (6 × 50mL) to remove residual DMF. The organic phase was collected, and concentrated under reduced pressure. The remaining DMF was removed from the viscous liquid using vacuum distillation, and the polymer dissolved in chloroform and dried over magnesium sulfate. The chloroform was removed under reduced pressure, and the resulting polymer placed in a vacuum desiccator for 16 h. This afforded pure poly(PYMP) (0.51 g). The purity of the material was confirmed using proton NMR, with the peaks in the region 4.1-4.8 ppm being due to the reacted and unreacted propargyl esters, The peaks in the region 2.4-3.2 ppm are due to the remaining protons in the poly(PYMP) molecule. Poly(PYMP) was characterized by
SEC using universal calibration to determine the molecular weights. \((M_n = 1944 \text{ g/mol, } M_w = 24495 \text{ g/mol, } M_p = 6670 \text{ g/mol})\). The poly(PYMP) was also characterized by IR spectroscopy, IR (KBr) \(\mu: 3282, 2933, 1732 \text{ cm}^{-1}\)

**Functionalization of poly(PYMP) to poly(Au-PYMP):** In a scintillation vial, poly(PYMP) (20 mg) and \([\text{Au(OH)}(\text{IPr})]\) (20.9 mg, 0.0347 mmol) were reacted in THF (1.5 mL). The reaction mixture was heated to 60\(^\circ\)C for 14h. After this time period, the mixture was allowed to cool to room temperature, THF was removed under vacuum and pentane (3 mL) was added. Solvent was again removed under vacuum. This operation was repeated three times to remove all residual THF and affords the poly(Au-PYMP) (40.4 mg in quantitative yield based on the stoichiometric loss of water). The poly(Au-PYMP) was characterized by IR spectroscopy, IR (KBr) \(\mu: 2962, 1731, 1470, 803, 758 \text{ cm}^{-1}\). The conversion of poly(PYMP) to poly(Au-PYMP) was confirmed by the disappearance of the stretch at 3282 cm\(^{-1}\), characteristic of the terminal alkyne C-H stretch in the poly(PYMP).

**Emission spectroscopy of poly(Au-PYMP):** The gold functionalized poly(Au-PYMP) (2.2 mg) was dissolved in DCM (13.31 g). This solution was transferred to a Schlenk tube, sealed with a rubber septum and degassed by performing 6 freeze pump thaw cycles. This solution was transferred via a cannula needle to a deoxygenated, sealed fluorescence cuvette. The spectroscopic properties of this poly(Au-PYMP) solution were analyzed by determining both an emission and excitation spectrum. Both the emission and excitation spectra were obtained using emission and excitation slit widths of 2.5 nm and a scan rate of 30 nm/min. The emission spectrum was obtained by using an excitation wavelength of 347 nm, scanning from 355 nm to 690 nm, The excitation spectrum was obtained by determining the magnitude of the emission at 382 nm, scanning from 300 to 375 nm. To confirm that the luminescence is a phosphorescence rather than fluorescence, a similar solution of poly(Au-PYMP) was prepared, although this second solution was not deoxygenated. This non-deoxygenated solution showed no emission spectrum when excited by 347 nm UV radiation under the same conditions as the deoxygenated sample. The luminescence properties of the poly(Au-PYMP) materials were qualitatively shown by preparing a separate solution of the poly(Au-PYMP). This solution was prepared by dissolving the poly(Au-PYMP) (2.2 mg) into DCM(13.29 g), and performing 6 freeze-
pump-thaw cycles. The luminescence of the functionalized poly(Au-PYMP) was qualitatively determined by placing the Schlenk tube containing the poly(Au-PYMP) solution under a Spectroline ENF-280C/FE lamp irradiating at 365 nm, and photographing the resulting blue-violet luminescence. The luminescence detector was calibrating with a solution of pyrene in cyclohexane, knowing the quantum yield of pyrene in cyclohexane (0.65).

**Determination of Quantum Yield:** Quantum yields were obtained by reference to pyrene as a standard. Solutions of pyrene (2.8mg/L) were prepared in cyclohexane and poly(Au-PYMP) (115 mg/L) in chloroform. Poly(Au-PYMP) and 25 mL chloroform were added to separate Schlenk tubes and subjected to 7 cycles of freeze pump thaw degassing. Poly(Au-PYMP) was then added to a quartz cuvette fitted with a rubber septum and an absorption spectra taken, with the absorption measured at 347 nm to ensure the absorption was in the range of 0.1, followed by a luminescence spectrum in the range 357-600 nm. A small amount of poly(Au-PYMP) solution was removed by cannula and replaced by degassed chloroform followed by the recording of the absorption and luminescence spectrum. This process was repeated with absorption spectra in the range of 0.1 to 0.02. Absorption spectra of pyrene were undertaken in a similar manner, although without degassing. Luminescence spectra were integrated from 357-600 nm and plotted against absorbance. The slopes of the zero-intercept samples of the two pyrene samples were cross-calibrated and compared with polyPYMP to determine the quantum yield according to the following equation:

\[
\Phi_{\text{poly(Au-PYMP)}} = \Phi_{\text{pyrene}} \frac{\text{slope}_{\text{poly(Au-PYMP)}}}{\text{slope}_{\text{pyrene}}} \left(\frac{n_{\text{chloroform}}}{n_{\text{cyclohexane}}}\right)^2
\]

Where \(\Phi_{\text{pyrene}}\) is the quantum yield of pyrene in cyclohexane, taken to be 0.65.\(^3\) \(\text{slope}_{\text{poly(Au-PYMP)}}\) is the slope of the integrated luminescence of the poly(Au-PYMP) against absorbance, \(\text{slope}_{\text{pyrene}}\) is the slope of the integrated luminescence of the pyrene against absorbance, \(n_{\text{chloroform}}\) is the refractive index of chloroform, and \(n_{\text{cyclohexane}}\) is the refractive index of cyclohexane.
**Luminescence Lifetime Measurement:** A sample of poly(Au-PYMP) in chloroform was prepared in chloroform at a concentration of 0.017 mg/mL. This sample was placed in a cuvette and degassed by several freeze-pump thaw cycles. The time decay of the luminescence was measured to deduce the excited state lifetime.

**Emission spectroscopy of poly(Au-PYMP):** The gold functionalized poly(Au-PYMP) (2.2 mg) was dissolved in chloroform (13.31 g). This solution was transferred to a Schlenk tube, sealed with a rubber septum and degassed by performing 6 freeze pump thaw cycles. This solution was transferred via a canula needle to a deoxygenated, sealed fluorescence cuvette. The spectroscopic properties of this poly(Au-PYMP) solution were analyzed by determining both an emission and excitation spectrum. Both the emission and excitation spectra were obtained using emission and excitation slit widths of 2.5 nm and a scan rate of 30 nm/min. The emission spectrum was obtained by using an excitation wavelength of 347 nm, scanning from 355 nm to 690 nm. The excitation spectrum was obtained by determining the magnitude of the emission at 382 nm, scanning from 300 to 375 nm. To confirm that the luminescence is a phosphorescence rather than fluorescence, a similar solution of poly(Au-PYMP) was prepared, although this second solution was not deoxygenated. This non-deoxygenated solution showed no emission spectrum when excited by 347 nm UV radiation under the same conditions as the deoxygenated sample. The same measurements were undertaken in dichloromethane, and the same spectra were obtained (see Figure below).
IR spectra of 1 and 3

poly(PYMP) 1

poly(Au-PYMP) 3
$^1$H NMR of Poly(Au-PYMP) 3

Emission and Excitation spectra of the poly(Au-PYMP) in DCM.

References