Electronic Supplementary Material (ESI) for Polymer Chemistry.

Synthesis and Characterization of a Ruthenium-Containing Copolymer for Use as a Photoredox Catalyst

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1) Materials and Methods

All chemicals were purchased from Sigma Aldrich, Alfa Aesar, Oakwood Chemicals, or TCI America, and used as received unless otherwise indicated. NMR spectroscopic characterization was conducted on a Bruker NEO-400 MHz spectrometer using $CDCl_3$, DMSO-d_6, or acetone-d_6. Chemical shifts are reported in ppm and referenced to the residual solvent. Compounds **1**[1], **2**[2], **3**[3], **4**[4], **5**[5], and $Ru(bpy)_2(dmbpy)(PF_6)_2$[6] were synthesized using modified procedures previously described in the literature. 1,3,5-trioxane was utilized as an internal standard to calculate conversion and yields of small-molecule transformations.

UV-Visible absorption spectra were obtained on a PerkinElmer LAMBDA 365 UV-Vis spectrometer (PerkinElmer, Inc) using a quartz cuvette (VWR). Luminescence spectra were obtained on a PerkinElmer FL 6500 (PerkinElmer, Inc) using a quartz cuvette (VWR). Solutions for UV-Vis and luminescence spectra were prepared in acetonitrile or dimethyl sulfoxide (Sigma-Aldrich, HPLC grade). DLS experiments of the poly[$Ru(bpy)_2(dmbpy)(PF_6)_2$-co-pyrene-co-MMA] polymer were performed using a Wyatt DynaPro NanoStar Dynamic Light-Scattering instrument at 298 K using a 2 microliter quartz cuvette. The polymer solutions for DLS were prepared at similar concentrations as they would be under the standard reaction conditions. The DLS data were processed by the DYNAMICS software to get an estimate for the hydrodynamic radius (Rh) of the polymer in acetonitrile and dimethyl sulfoxide based on the intensity distribution of particle sizes.

Photoredox experiments were conducted using Kessil LED photoredox lights (456 nm; PR160) using 1 dram vials with septa. All reactions were irradiated using two Kessil PR160 LEDs at a vial-to-lamp distance of 6 cm with a cooling fan positioned adjacent to the reactions (household desk fan). More information and specifics can be found at: https://kessil.com/support/downloads.php.

2) General Procedure for C–H Arylation Reactions and Control Reactions

With poly[Ru(bpy)$_2$(dmbpy)(PF$_6$)$_2$-co-pyrene-co-MMA]: In a 1-dram vial with a septum, the aryl bromide (0.1 mmol), corresponding trapping agent (1.0 mmol), poly[Ru(bpy)$_2$(dmbpy)(PF$_6$)$_2$-co-pyrene-co-MMA] (0.002 mmol Ru(bpy)$_2$(dmbpy)(PF$_6$)$_2$ based on weight% of Ru(bpy)$_2$(dmbpy)(PF$_6$)$_2$ in the copolymer), and DIPEA (0.14 mmol) were dissolved in 0.5 mL of dry d$_6$-DMSO. The resulting mixture was sparged with nitrogen and a vent needle for 15-20 minutes. The needles were removed, and the septum was sealed with electrical tape. The vial was then placed between two 456 nm Kessil PR160 LEDs with a vial-to-lamp distance of 6 cm, and irradiated with stirring for 16-32 h. 1,3,5-trioxane was added and the yield was calculated by ^{1}H-NMR spectroscopy.

With small molecule Ru(bpy)$_3$(PF$_6$)$_2$ and small molecule pyrene: In a 1-dram vial with a septum, 2-bromobenzonitrile (0.1 mmol), N-methyl pyrrole (1.0 mmol), Ru(bpy)$_3$(PF$_6$)$_2$ (0.002 mmol), pyrene (0.005 mmol), and DIPEA (0.14 mmol) were dissolved in 0.5 mL of dry d$_6$-DMSO or d$_3$-MeCN. The resulting mixture was sparged with nitrogen and a vent needle for 15-20 minutes. The needles were removed, and the septum was sealed with electrical tape. The vial was then placed between two 456 nm Kessil PR160 LEDs with a vial-to-lamp distance of 6 cm, and irradiated with stirring for 3 h. 1,3,5-trioxane was added and the yield was calculated by ^{1}H-NMR spectroscopy.

With poly[Ru(bpy)$_2$(dmbpy)(PF$_6$)$_2$-co-MMA] and poly[pyrene-co-MMA]: In a 1-dram vial with a septum, 2-bromobenzonitrile (0.1 mmol), N-methyl pyrrole (1.0 mmol), poly[Ru(bpy)$_2$(dmbpy)(PF$_6$)$_2$-co-MMA] (0.002 mmol Ru(bpy)$_2$(dmbpy)(PF$_6$)$_2$ based on weight% of Ru(bpy)$_2$(dmbpy)(PF$_6$)$_2$ in the copolymer), poly[pyrene-co-MMA] (0.004 mmol pyrene based on weight% of pyrene in the copolymer), and DIPEA (0.14 mmol) were dissolved in 0.5 mL of dry d$_6$-DMSO. The resulting mixture was sparged with nitrogen and a vent needle for 15-20 minutes. The needles were removed, and the septum was sealed with electrical tape. The vial was then placed between two 456 nm Kessil PR160 LEDs with a vial-to-lamp distance of 6 cm, and irradiated with stirring for 16 h. 1,3,5-trioxane was added and the yield was calculated by ^{1}H-NMR spectroscopy.

With Ru(bpy)$_2$(dmbpy-MMA)(PF$_6$)$_2$ and pyrene-MMA monomers: In a 1-dram vial with a septum, 2-bromobenzonitrile (0.1 mmol), N-methyl pyrrole (1.0 mmol), Ru(bpy)$_2$(dmbpy-MMA)(PF$_6$)$_2$ (0.002 mmol), pyrene-MMA (0.004 mmol), and DIPEA (0.14 mmol) were dissolved in 0.5 mL of dry d$_6$-DMSO. The resulting mixture was sparged with nitrogen and a vent needle for 15-20 minutes. The needles were removed, and the septum was sealed with electrical tape. The vial was then placed between two 456 nm Kessil PR160 LEDs with a vial-to-lamp distance of 6 cm, and irradiated with stirring for 16 h. 1,3,5-trioxane was added and the yield was calculated by ^{1}H-NMR spectroscopy.

3) Synthesis of Monomers

Synthesis of (4'-methyl-[2,2'-bipyridin]-4-yl)methanol (1)

4,4'-Dimethyl-2,2'-bipyridine (6.15 g, 33.3 mmol) and selenium dioxide (6.15 g, 55.5 mmol) were added 300 mL of 1,4-dioxane. The mixture was refluxed at 110°C for 24 hours. After cooling to room temperature, the mixture was filtered and the 1,4-dioxane was removed under reduced pressure. The solid was suspended in 300 mL of chloroform, filtered, and the chloroform removed under reduced pressure. 50 mL of methanol was added to the solid and the mixture was stirred on ice. $NaBH_4$ (1.0 g in 8.8 mL of 0.2M $NaOH_{(aq)}$) was added dropwise with stirring. The solution was stirred on ice for 30 minutes then warmed to room temperature and stirred for 2 hours. The methanol was removed under reduced pressure and 24 mL of saturated sodium bicarbonate was added. The aqueous phase was extracted with chloroform (4 x 80 mL), washed with brine (1 x 100 mL), dried over Na_2SO_4, and concentrated. The solid was purified by flash column chromatography (silica, 5% MeOH:CH_2Cl_2) to yield 3.12 g (47%) of **1** as a white solid. ^1H NMR (400 MHz, $CDCl_3$): δ=8.63 (d, 1H), 8.52 (d, 1H), 8.34 (s, 1H), 8.22 (s, 1H), 7.33 (d, 1H), 7.14 (d, 1H), 4.81 (s, 2H), 2.58 (s, 1H), 2.44 (s, 3H) ppm

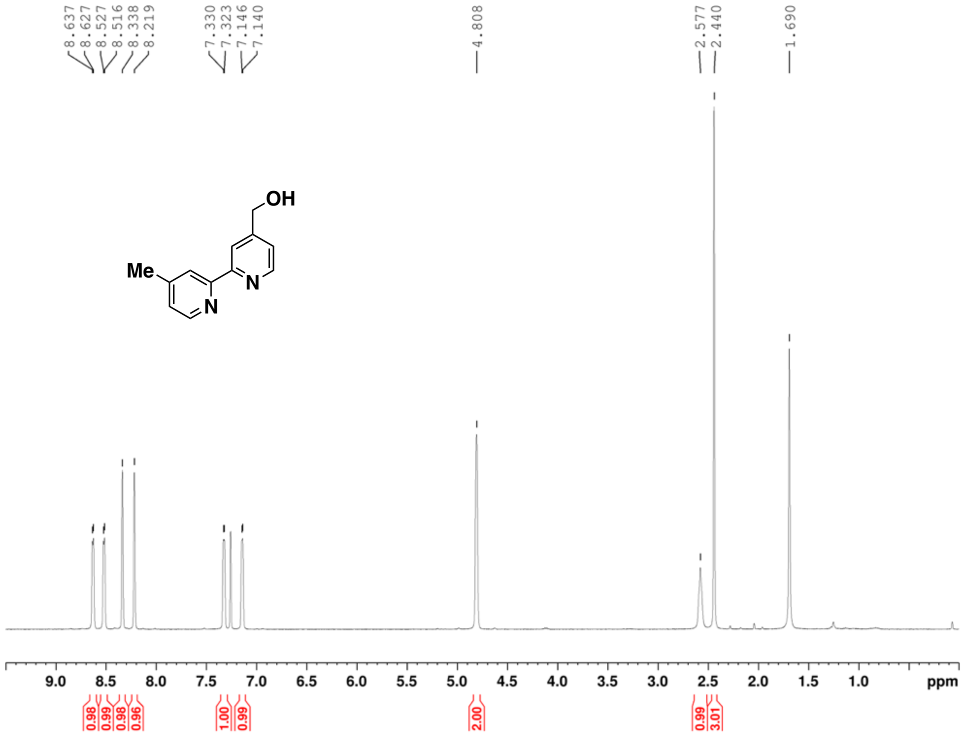


Figure S1. ^1H NMR spectrum of **1** ($CDCl_3$, 400 MHz)

Synthesis of (4'-methyl-[2,2'-bipyridin]-4-yl)methyl methacrylate (2)

1 (3.00 g, 15.0 mmol) and triethylamine (2.33 mL, 16.7 mmol) was added to 18 mL of chloroform with stirring. The solution was cooled to 0°C using an ice bath. Methacryloyl chloride (1.64 mL, 16.5 mmol) was added dropwise to the solution with stirring. After complete addition, the solution was stirred at room temperature for 24 hours. The organic layer was washed with distilled water (3 x 50 mL), saturated sodium bicarbonate (3 x 30 mL), brine (1 x 50 mL), and then dried over Na_2SO_4. A brown oil was obtained after concentration which was purified by flash column chromatography (silica, 5% MeOH:CH_2Cl_2) to yield 3.42 g (85%) of **2** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.67 (d, 1H), 8.54 (d, 1H), 8.38 (s, 1H), 8.23 (s, 1H), 7.30 (d, 1H), 7.15 (d, 1H), 6.23 (s, 1H), 5.65 (s, 1H), 5.29 (s, 2H), 2.44 (s, 3H), 2.01 (s, 3H) ppm

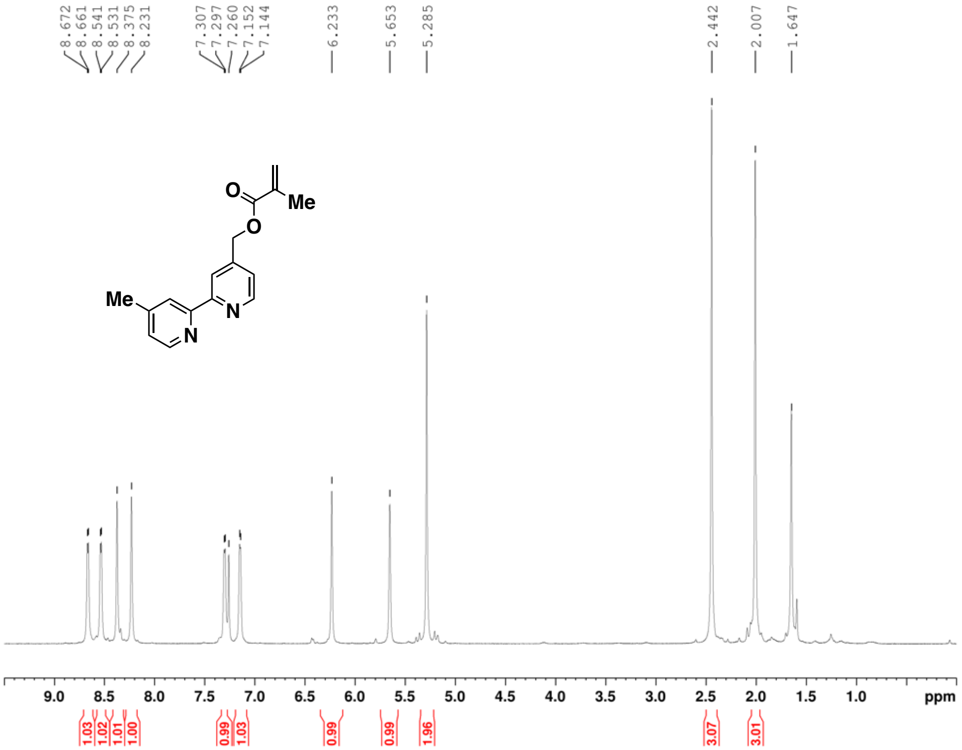


Figure S2. ^{1}H NMR spectrum of **2** ($CDCl_3$, 400 MHz)

Synthesis of cis-Bis(2,2'-bipyridine)dichlororuthenium(II) hydrate (3)

$RuCl_3$•$3H_2O$ (4.883 g, 18.7 mmol), bipyridine (5.87 g, 37.6 mmol), and LiCl (5.26 g) were added to a round bottom flask with 30 mL of dimethylformamide with stirring. The mixture was refluxed for 8 hours. The flask was cooled to room temperature, and 150 mL of acetone was added. The resultant solution was cooled to 0°C overnight. Filtering the solution yielded a dark green-black crystalline product. The crystals were washed with water (3 x 20 mL) and diethyl ether (3 x 20 mL) and then dried under reduced pressure yielding a dark green-black crystalline product; 5.41 g (60%).

Synthesis of Ru(bpy)$_2$(4-methacryloylmethyl-4'-methylbpy)$^{2+}$(PF6$^-$)$_2$ (4)

3 (5.34 g, 11.0 mmol) was added to a round bottom flask with 210 mL of ethanol while stirring. **2** (2.5 g, 9.3 mmol) was added, and the mixture was refluxed 22 hours. The flask was cooled to room temperature and the ethanol was removed under reduced pressure. 150 mL of distilled water was added with stirring. Potassium hexafluorophosphate (2.0 g, 11 mmol) was added to the mixture at which an orange precipitate was observed. The mixture was stirred for an additional hour, and the precipitate was filtered. The powder was washed with water (3 x 50 mL) and dried under reduced pressure to give 8.79 g (88%) of the orange product. ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.83 (d, 5H), 8.71 (s, 1H), 8.16 (t, 4H), 7.73 (m, 5H), 7.53 (m, 6H), 7.38 (d, 1H), 6.17 (s, 1H), 5.80 (t, 1H), 5.40 (s, 2H), 2.53 (s, 3H), 1.94 (s, 3H) ppm

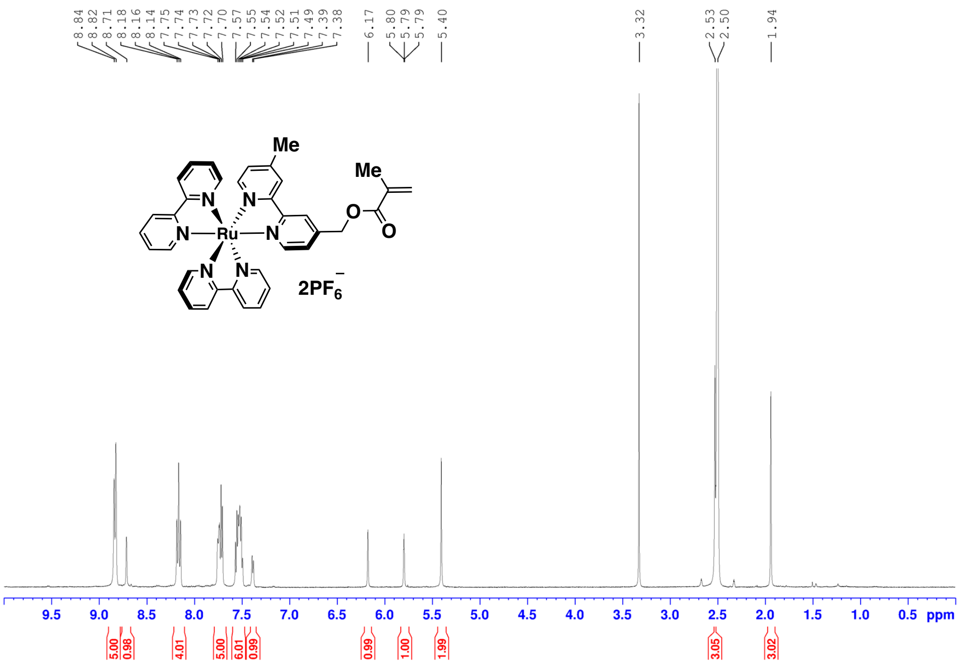


Figure S3. ^{1}H NMR spectrum of **4** (DMSO-d_6, 400 MHz)

Synthesis of pyren-1-ylmethyl methacrylate (5)

In a 250 mL round bottom flask, 1-pyrenemethanol (1.251 g, 5.39 mmol) and triethylamine (2.25 mL, 16.1 mmol) were added to 60 mL of dichloromethane with stirring. The solution was cooled to 0°C using an ice bath. Methacryloyl chloride (1.6 mL, 16.1 mmol) was added dropwise to the solution with stirring. After complete addition, the solution was stirred at room temperature for 24 hours. The organic layer was washed with distilled water (3 x 50 mL), saturated sodium bicarbonate (3 x 20 mL), brine (1 x 50 mL), and then dried over Na_2SO_4. A brown oil was obtained after concentration which was purified by flash column chromatography (silica, 10% EtOAc:hexanes) to yield 1.21 g (75%) of **5** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.24-8.16 (m, 4H), 8.11-8.01 (m, 4H), 6.15 (s, 1H), 5.92 (s, 2H), 5.57 (t, 1H), 1.97 (s, 3H) ppm

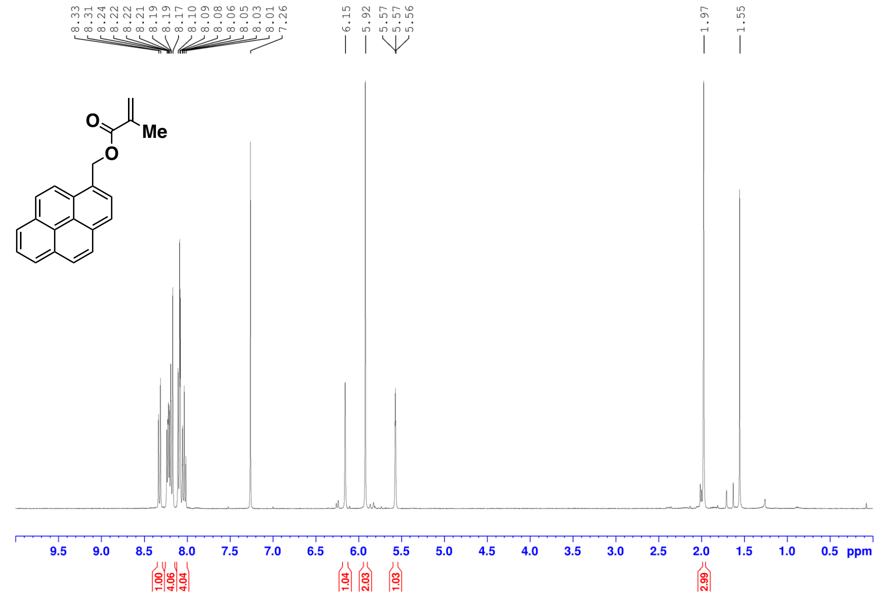


Figure S4. ^{1}H NMR spectrum of **5** (CDCl$_3$, 400 MHz)

4) Polymerization Procedures

Poly[Ru(bpy)$_2$(dmbpy)(PF$_6$)$_2$-co-pyrene-co-MMA]

4-Cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (20 mg, 0.05 mmol), 2,2′-azobis(2-methylpropionitrile) (2 mg, 0.01 mmol), **4** (0.539 g, 0.55 mmol), **5** (0.668 g, 2.22 mmol), methyl methacrylate (0.296 mL, 2.78 mmol), and dimethylformamide (2.2 mL) were added to a 20 mL scintillation vial with a septum. The solution was sparged with nitrogen and a vent needle for 15-20 minutes. The needles were removed, and electrical tape was used to seal the septum. The mixture was stirred at 75°C for 24 hours, after which the vial was cooled to room temperature. The solution was poured into 100 mL of cold methanol. The precipitate was filtered and washed with methanol (2 x 20 mL). The polymer was dried under reduced pressure, dissolved in a minimal amount of acetone, and precipitated into 100 mL of cold diethyl ether. The precipitate was filtered and dried under reduced pressure to yield 0.908 g of a red-orange powder.

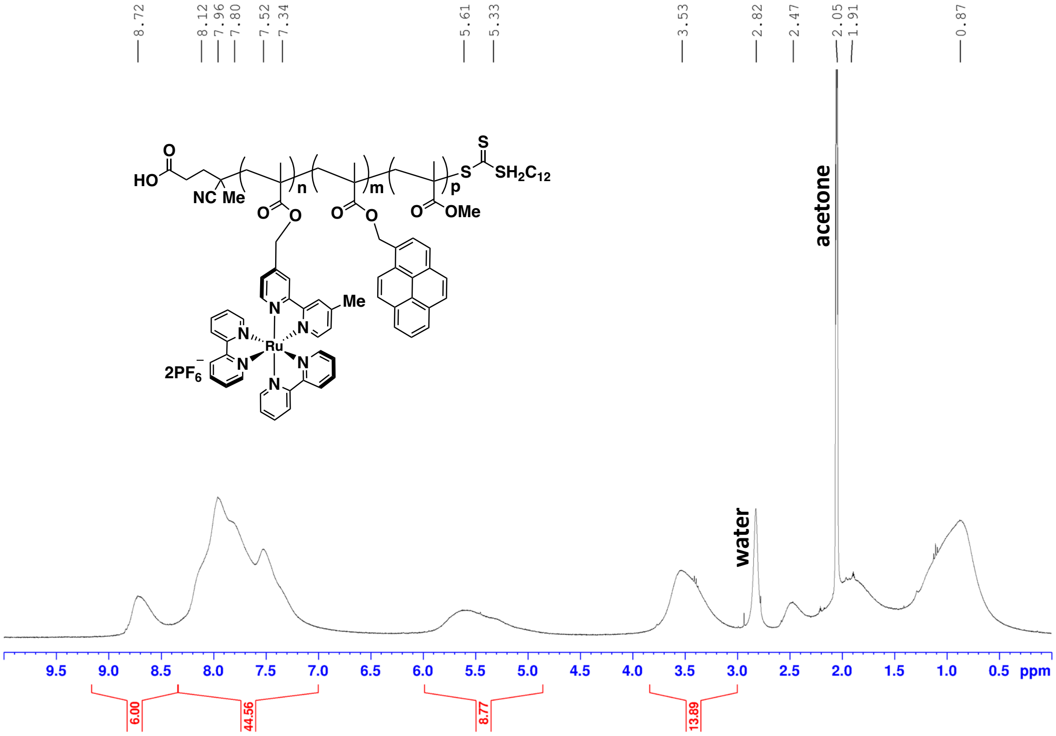


Figure S5. ^{1}H NMR spectrum of poly[Ru(bpy)$_2$(dmbpy)(PF$_6$)$_2$-co-pyrene-co-MMA] (acetone-d$_6$, 400 MHz)

Poly[Ru(bpy)$_2$(dmbpy)(PF$_6$)$_2$-co-MMA]

4-Cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (10 mg, 0.025 mmol), 2,2′-azobis(2-methylpropionitrile) (1 mg, 0.005 mmol), **4** (0.385 g, 0.40 mmol), methyl methacrylate (0.38 mL, 3.57 mmol), and dimethylformamide (1.1 mL) were added to a 1 dram vial with a septum. The solution was sparged with nitrogen and a vent needle for 15-20 minutes. The needles were removed, and electrical tape was used to seal the septum. The mixture was stirred at 75°C for 24 hours, after which the vial was cooled to room temperature. The solution was poured into 50 mL of cold methanol. The precipitate was filtered and washed with methanol (2 x 10 mL). The polymer was dried under reduced pressure, dissolved in a minimal amount of acetone, and precipitated into 50 mL of cold diethyl ether. The precipitate was filtered and dried under reduced pressure to yield 0.425 g of a red-orange powder.

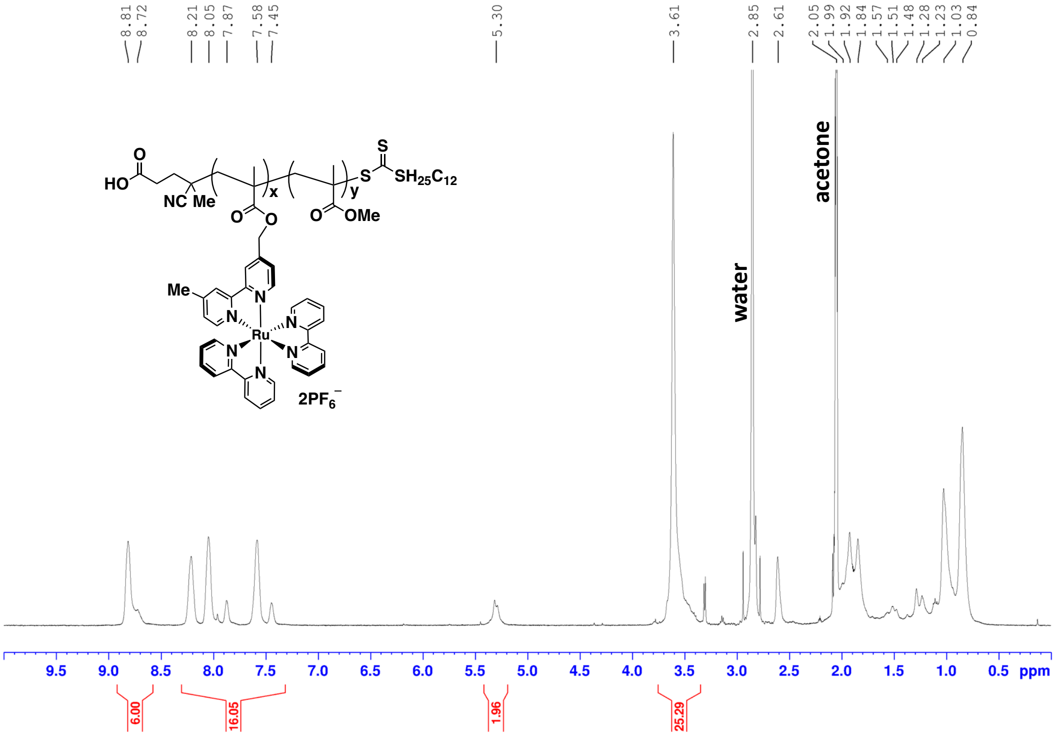


Figure S6. ^{1}H NMR spectrum of poly[Ru(bpy)$_2$(dmbpy)(PF$_6$)$_2$-co-MMA] (acetone-d$_6$, 400 MHz)

Poly[pyrene-co-MMA]

4-Cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (25 mg, 0.062 mmol), 2,2'-azobis(2-methylpropionitrile) (2 mg, 0.01 mmol), **5** (0.101 g, 0.35 mmol), methyl methacrylate (1.21 mL, 11.36 mmol), and dimethylformamide (2.7 mL) were added to a 1 dram vial with a septum. The solution was sparged with nitrogen and a vent needle for 15-20 minutes. The needles were removed, and electrical tape was used to seal the septum. The mixture was stirred at 75°C for 24 hours, after which the vial was cooled to room temperature. The solution was poured into 50 mL of cold methanol. The precipitate was filtered and washed with methanol (2 x 10 mL). The polymer was dried under reduced pressure, dissolved in a minimal amount of acetone, and precipitated into 50 mL of cold diethyl ether. The precipitate was filtered and dried under reduced pressure to yield 0.844 g of a white powder.

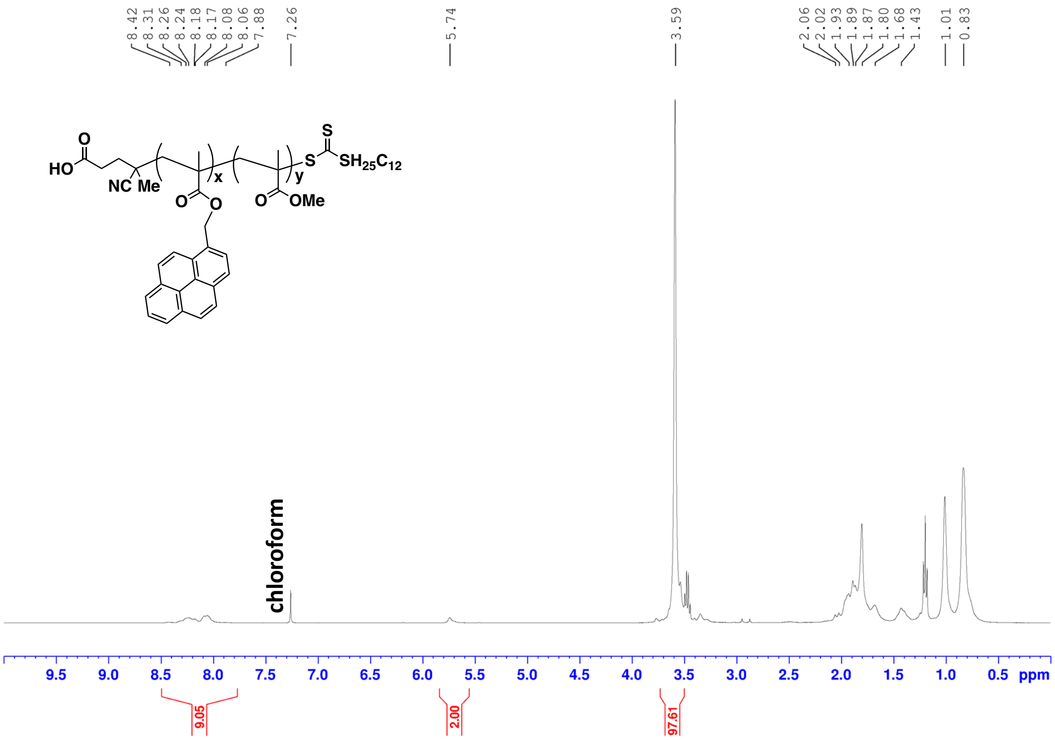
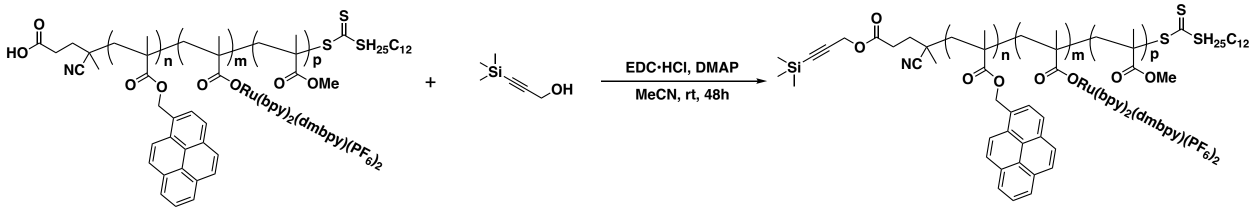


Figure S7. ^{1}H NMR spectrum of poly[pyrene-co-MMA] (CDCl$_3$, 400 MHz)

5) Chain-End Analysis of Polymer for Molecular Weight Determination

Post-Polymerization Functionalization with 3-trimethylysilylpropargyl Alcohol:



Scheme 1. Post-polymerization functionalization of carboxylic acid chain end with 3-trimethylysilylpropargyl alcohol

Poly[$\mathrm{Ru(bpy)_2(dmbpy)(PF_6)_2}$-co-pyrene-co-MMA] polymer (30 mg) and 3-trimethylsilylpropargyl alcohol (4.4 μL, 30 eq of hypothetical –COOH group) was dissolved in 200 μL of acetonitrile in a small vial. N-(3-Dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (0.19 mg, 1.5 eq of hypothetical –COOH group) and 4-(dimethylamino)pyridine (0.012 mg, 0.1 eq of hypothetical –COOH group) were added via stock solutions to the stirring reaction mixture, the N-(3-Dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride was added in portions of 1 equivalent at the start, and 0.5 eq after 24 hours of stirring. The solution was stirred for a total of 48 hours at room temperature after which the acetonitrile was removed by a nitrogen stream. DCM (10 mL) was added to the solution and washed with distilled water (4 x 5 mL). The organic layer was separated and precipitated into an excess of diethyl ether to remove any unreacted small molecules. The polymer was collected and dried under reduced pressure.

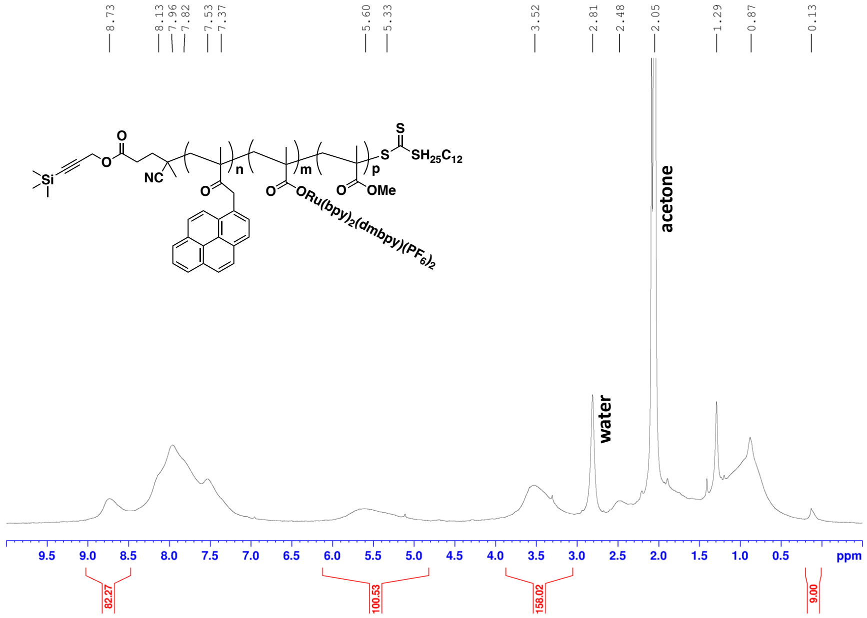


Figure S8. ^{1}H NMR spectrum of 3-trimethylsilylpropargyl-functionalized poly[$\mathrm{Ru(bpy)_2(dmbpy)(PF_6)_2}$-co-pyrene-co-MMA] (acetone-d_6, 400 MHz)

Percent incorporation was calculated by calibrating the –TMS singlet at 0.13 ppm in Figure S7 to the theoretical value of 9. The ratios of the actual over theoretical integrations of $Ru(bpy)_2(dmbpy)(PF_6)_2$ and pyrene were calculated as shown below. The actual integration of the pyrene methylene hydrogens was determined by subtracting the theoretical integration of the $Ru(bpy)_2(dmbpy)(PF_6)_2$ methylene hydrogens. The molecular weight was calculated by multiplying the actual incorporation numbers by their respective monomer molecular weights, the summation of those values is calculated to be the molecular weight of the polymer.

$$Incorporation\ [\mathrm{Ru(bpy)_2(dmbpy)}(PF_6)_2] = \frac{82.27}{6} = 13.7$$

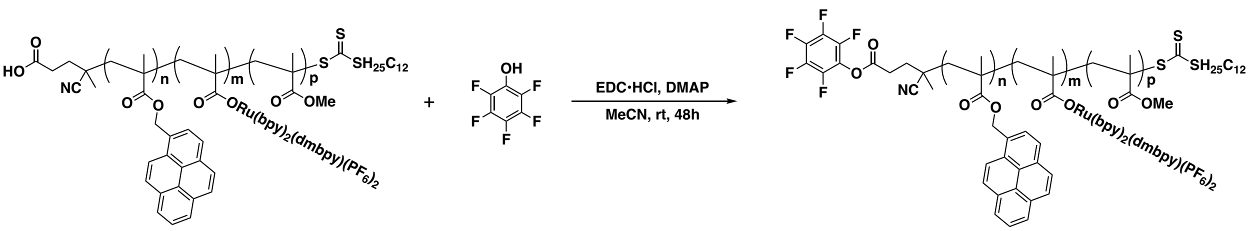
$$Incorporation\ (pyrene) = \frac{100.53 - (13.7\ \times\ 2)}{2} = 36.6$$

$$Incorporation\ (MMA) = \frac{158.02}{3} = 52.7$$

Incorporation number (m, n, p): 13.7 (Ruthenium complex), 36.6 (Pyrene), 52.7 (MMA)

$$M_{\mathrm{n}} = (13.7 \times 971.68) + (36.6 \times 300.36) + (52.7 \times 100.12) = 29581\ Da\ (\sim 29.6\ kDa)$$

Post-Polymerization Functionalization with Pentafluorophenol:



Scheme 2. Post-polymerization functionalization of carboxylic acid chain end with pentafluorophenol

Poly[$Ru(bpy)_2(dmbpy)(PF_6)_2$-co-pyrene-co-MMA] polymer (30 mg) and pentafluorophenol (5.5 mg, 30 eq of hypothetical –COOH group) was dissolved in 200 µL of acetonitrile in a small vial. N-(3-Dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (0.19 mg, 1.5 eq of hypothetical –COOH group) and 4-(dimethylamino)pyridine (0.012 mg, 0.1 eq of hypothetical –COOH group) were added via stock solutions to the stirring reaction mixture, the N-(3-Dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride was added in portions of 1 equivalent at the start, and 0.5

eq after 24 hours of stirring. The solution was stirred for a total of 48 hours at room temperature after which the acetonitrile was removed by a nitrogen stream. DCM (10 mL) was added to the solution and washed with distilled water (4 x 5 mL). The organic layer was separated and precipitated into an excess of diethyl ether to remove any unreacted small molecules. The polymer was collected and dried under reduced pressure.

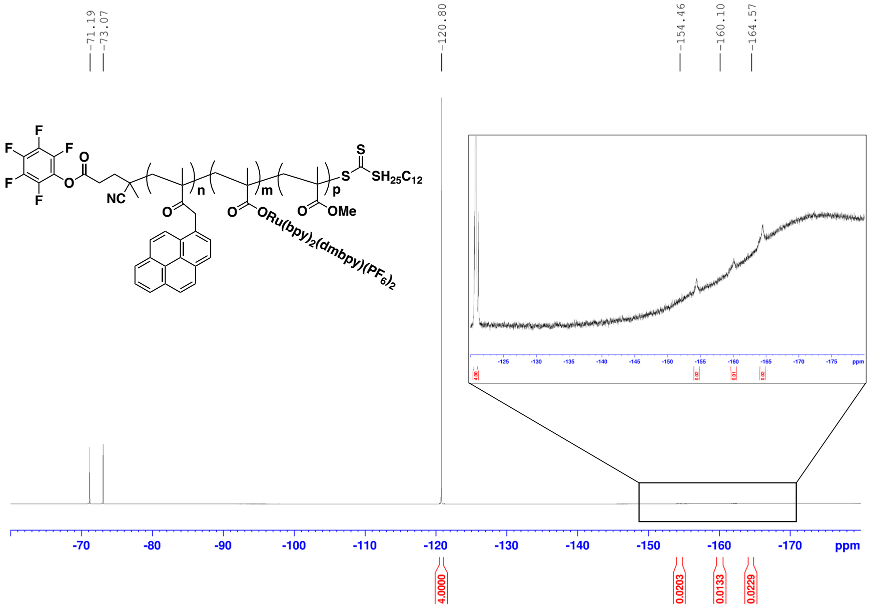


Figure S9. ^{19}F NMR spectrum of pentafluorophenol-functionalized poly[Ru(bpy)$_2$(dmbpy)(PF$_6$)$_2$-co-pyrene-co-MMA] (acetone-d$_6$, 400 MHz)

Molecular weight was calculated by first weighing out an amount of polymer into a vial and recording the mass on an analytical balance. Using 1,4-diiodotetrafluorobenzene as an internal standard, the number of moles of the polymer was calculated using the three peaks with chemical shifts of -154.46, -160.10, and -164.57 ppm in the ^{19}F-NMR spectrum using the equation:

$$\frac{n_p}{n_{is}} = \frac{\left(\frac{I_p}{N_p}\right)}{\left(\frac{I_{is}}{N_{is}}\right)}$$

Where:
I_p = integration of the selected peak of polymer
I_{is} = integration of the selected peak of internal standard
n_p = number of moles of polymer
n_{is} = number of moles of internal standard
N_p = number of fluorines corresponding to the chosen peak of product
N_{is} = number of fluorines corresponding to the chosen peak of internal standard

$$M_{\mathrm{n}} = \frac{m_p}{n_p}$$

Where:
m_p = mass of polymer
n_p = number of moles of polymer

$$Average\ M_{\mathrm{n}} = \frac{(32724 + 30679 + 28753)}{3} = 30715\ Da\ (\sim 31\ kDa)$$

6) Photophysical Measurements

Table S1. Photophysical properties of Ru(II) and pyrene species used in this study in DMSO. The molar extinction coefficient is given of the absorption maxima. The singlet energies of the Ru(II) species are estimated from the absorption maxima. The singlet energies of the pyrene species were determined by fitting their fluorescence spectra. The triplet energies of the Ru(II) species were determined by fitting their phosphorescence spectra.

Species	**Absorption Maxima (nm)**	**$\varepsilon_{\text{absorption maxima}}$ (M^{-1} cm^{-1})**	**singlet energy (kJ/mol, eV)**	**triplet energy (kJ/mol, eV)**
Pyrene	339	46736	319, 3.31	–
Pyrene-MMA	346	35774	316, 3.27	–
Ru(bpy)$_2$(dmbpy)	457	10375	262, 2.71	193, 2.00
Ru(bpy)$_2$(dmbpy-MMA)	457	18454	262, 2.71	193, 2.00
Poly[Ru(bpy)$_2$(dmbpy)(PF$_6$)$_2$-co-MMA	457	12565	262, 2.71	193, 2.00
Poly[pyrene-co-MMA]	346	3386	316, 3.27	–
Poly[Ru(bpy)$_2$(dmbpy)(PF$_6$)$_2$-co-pyrene-co-MMA]	458 (Ru), 344 (Py)	9351 (Ru), 25195 (Py)	261, 2.71 (Ru) 316, 3.27 (Py)	193, 2.00 (Ru)

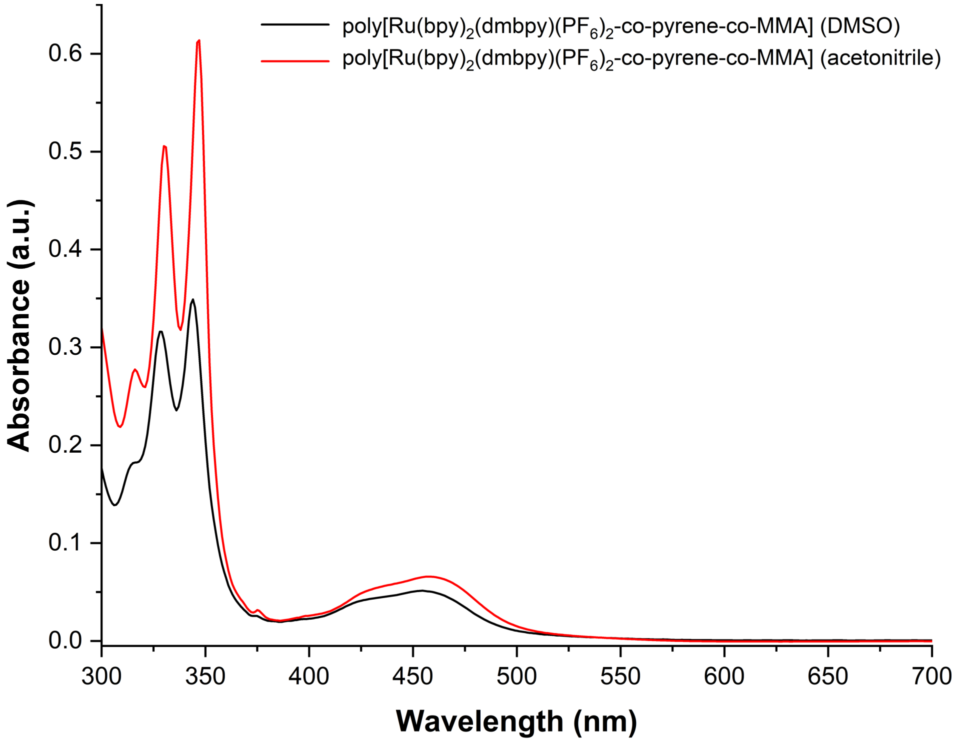


Figure S10. UV-Vis spectra of poly[Ru(bpy)$_2$(dmbpy)(PF$_6$)$_2$-co-pyrene-co-MMA] in acetonitrile and DMSO

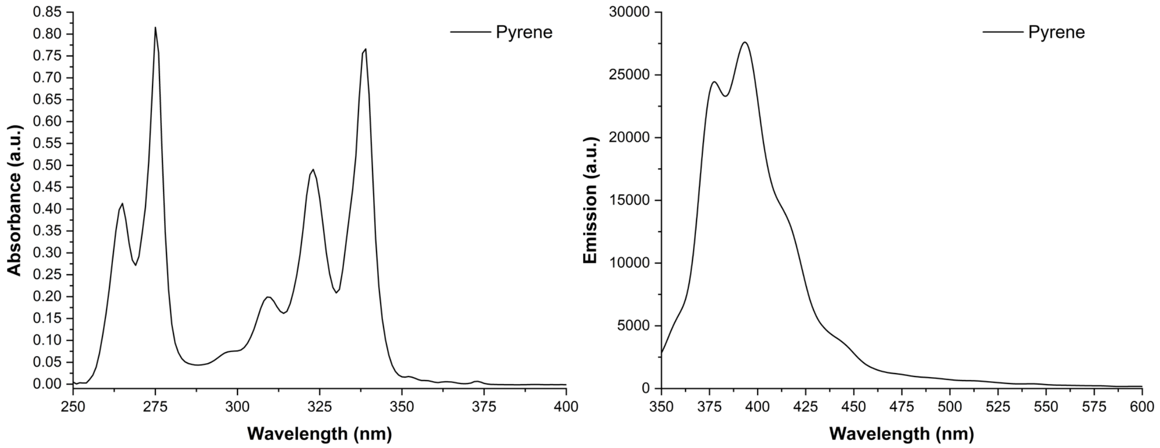


Figure S11. (Left) UV/Vis spectrum and (right) fluorescence spectrum of pyrene in DMSO; excitation wavelength = 335 nm.

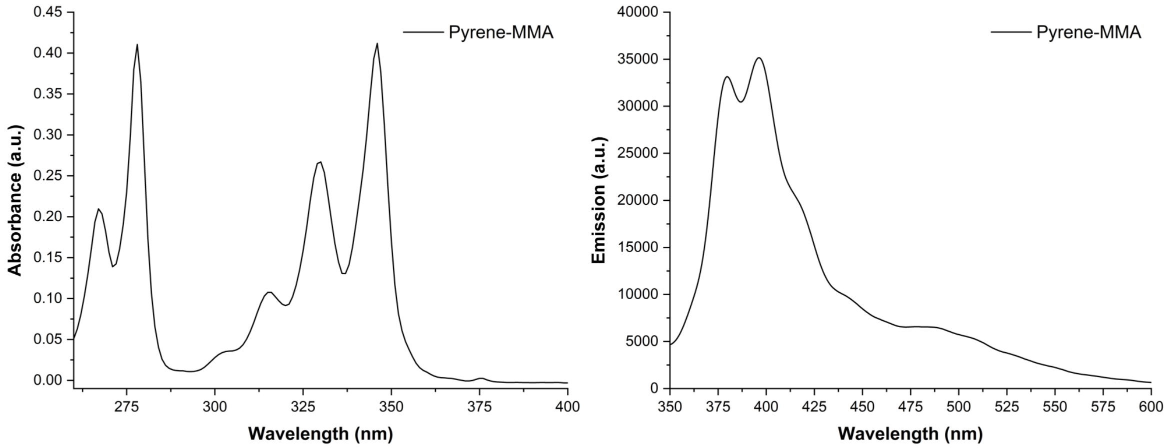


Figure S12. (Left) UV/Vis spectrum and (right) fluorescence spectrum of pyrene-MMA in DMSO; excitation wavelength = 335 nm.

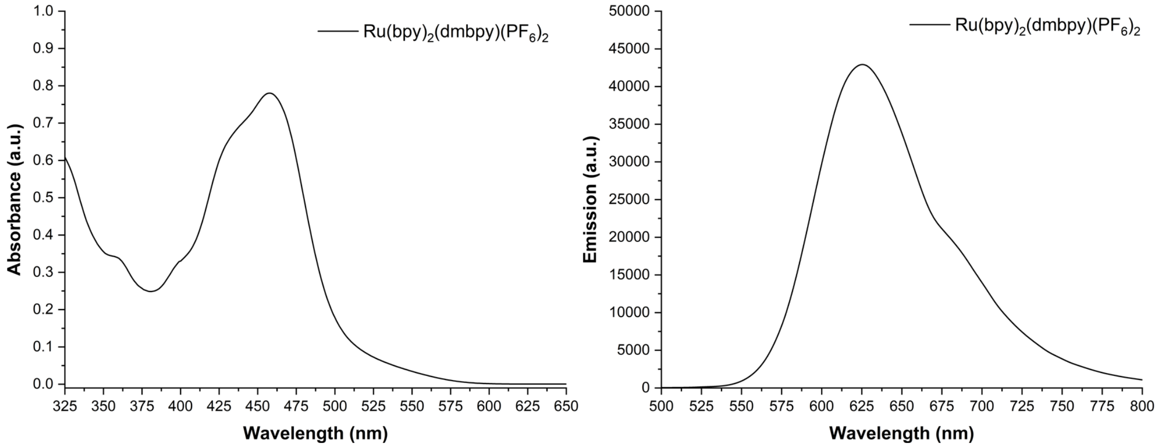


Figure S13. (Left) UV/Vis spectrum and (right) phosphorescence spectrum of Ru(bpy)$_2$(dmbpy)(PF$_6$)$_2$ in DMSO; excitation wavelength = 455 nm.

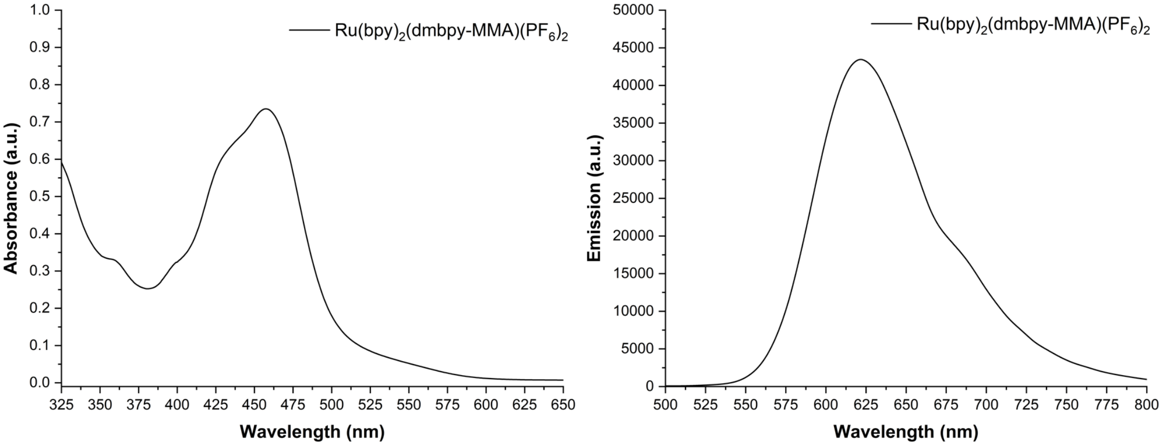


Figure S14. (Left) UV/Vis spectrum and (right) phosphorescence spectrum of Ru(bpy)$_2$(dmbpy-MMA)(PF$_6$)$_2$ in DMSO; excitation wavelength = 455 nm.

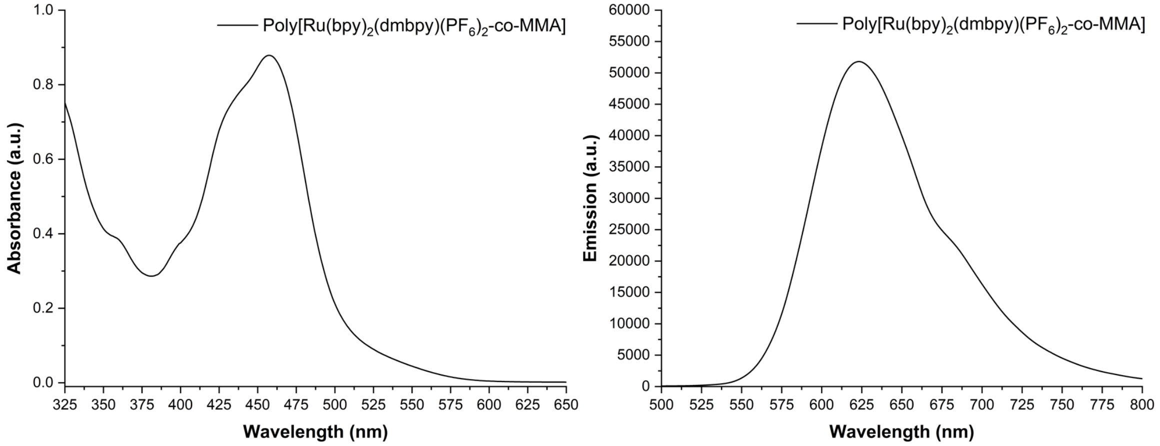


Figure S15. (Left) UV/Vis spectrum and (right) phosphorescence spectrum of poly[Ru(bpy)$_2$(dmbpy)(PF$_6$)$_2$-co-MMA] in DMSO; excitation wavelength = 455 nm.

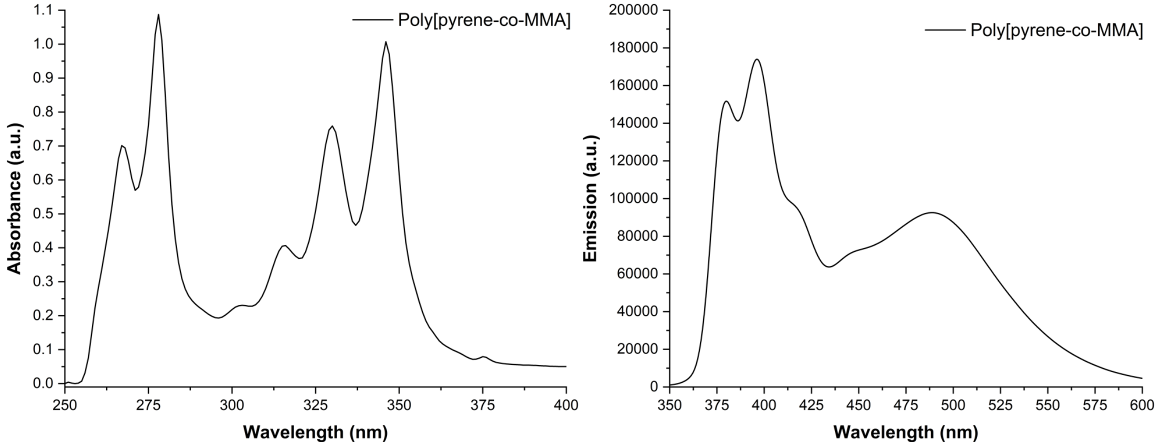


Figure S16. (Left) UV/Vis spectrum and (right) fluorescence spectrum of poly[pyrene-co-MMA] in DMSO; excitation wavelength = 335 nm.

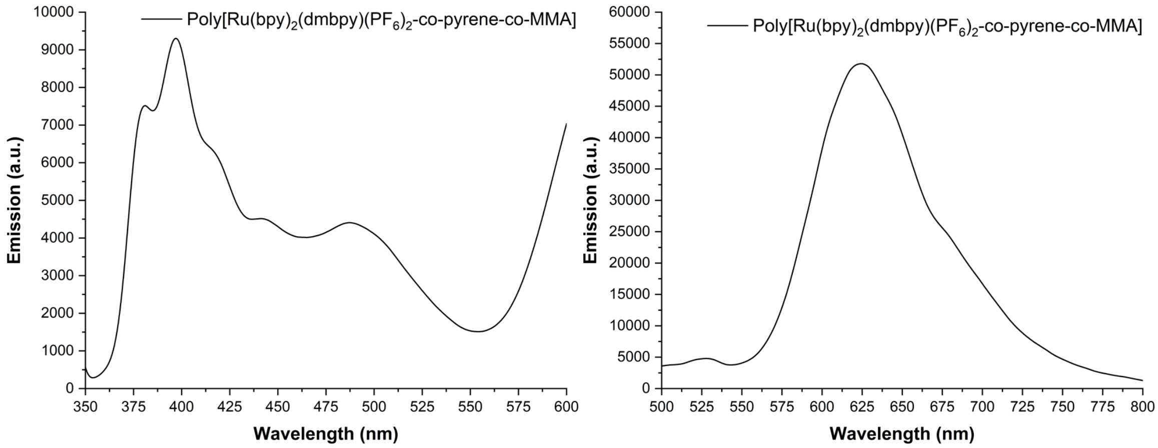


Figure S17. Luminescence spectra of poly[Ru(bpy)$_2$(dmbpy)(PF$_6$)$_2$-co-pyrene-co-MMA] with excitation wavelength of (left) 335 nm light and (right) 455 nm light in DMSO.

The molar absorptivity coefficients were found by first dissolving a known quantity of each of the Ru(II) and pyrene species in a known volume of DMSO. Their UV/Vis spectra were then recorded, ensuring that the concentration used kept the absorbance below 1 a.u. In the case of copolymers, the concentration of the Ru(II) and pyrene groups was determined by back calculating their quantities based on the weight percentage of each species obtained from ^{1}H-NMR analysis. By applying the Beer-Lambert law, the molar absorptivity coefficients were determined:

$$A = \epsilon c l$$

The singlet energies of the pyrene species and the triplet energies of the Ru(II) species were determined by application of a one mode Franck-Condon analysis of the room temperature emission spectra as previously described in literature.[7]

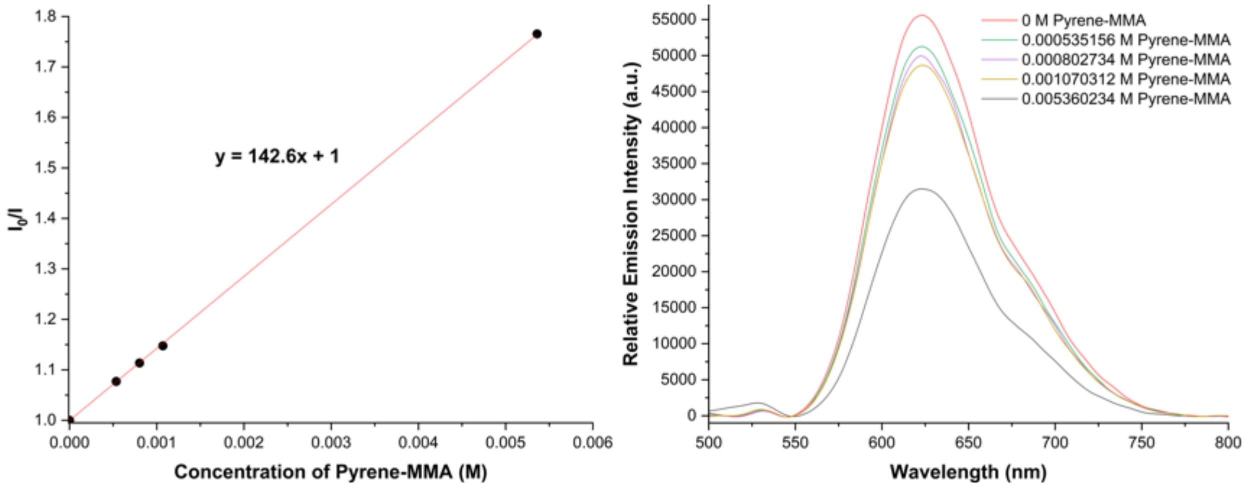


Figure S18. Stern-Volmer plot for the quenching of [Ru(bpy)$_2$(dmbpy)](PF$_6$)$_2$ in poly[Ru(bpy)$_2$(dmbpy)(PF$_6$)$_2$-co-MMA] by pyrene-MMA.

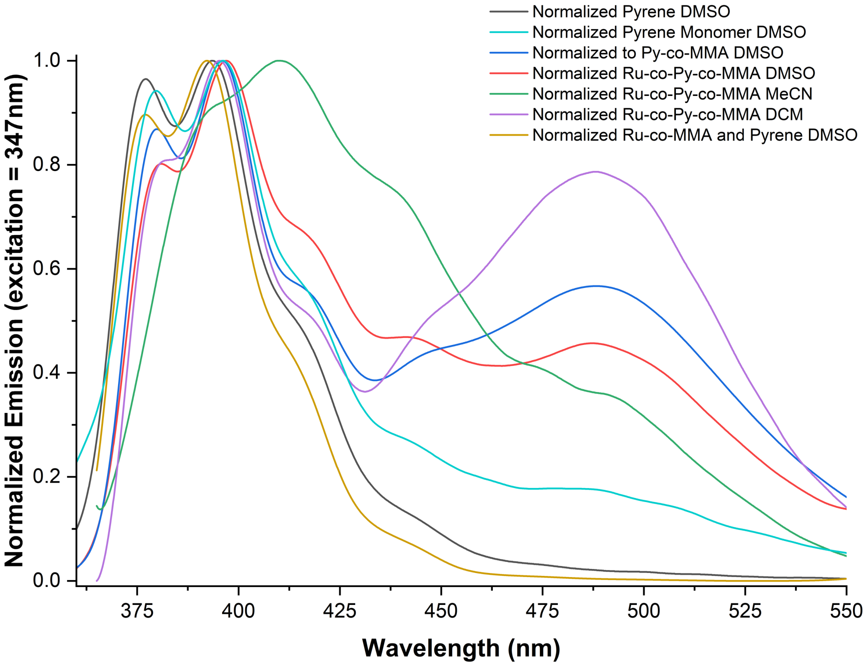


Figure S19. Normalized emission spectra of pyrene species used in this study in various solvents; excitation wavelength = 335 nm. The spectral range is cut off at 550 nm to bypass the emission from the Ru(II) species. The pyrene excimer emission is observed centered at ~488 nm. The prominent and intense excimer peak within the spectrum of poly[Ru(bpy)$_2$(dmbpy)(PF$_6$)$_2$-co-pyrene-co-MMA] in DCM was of interest for a reaction solvent. However, the copolymer has very limited solubility within DCM at the typical reaction concentrations, therefore, only trace amounts of product were observed.

7) Photodegradation Studies

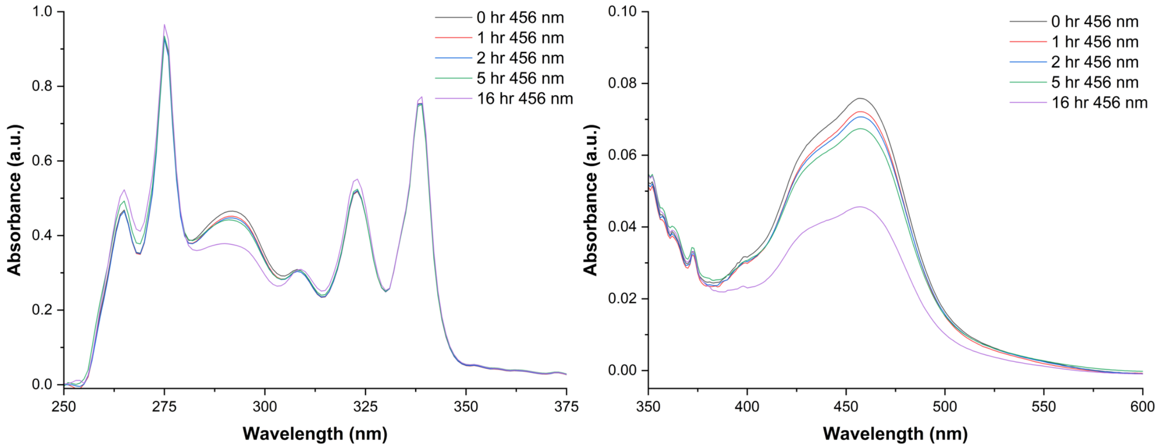


Figure S20. Relative UV/Vis spectra during the photodecomposition of Ru(bpy)$_2$(dmbpy)(PF$_6$)$_2$ and pyrene dissolved under reaction conditions in DMSO under nitrogen without the presence of substrate, trapping agent, or DIPEA and exposed to 456 nm LEDs over 16 hours with stirring. The MLCT absorbances of the Ru(II) species (centered ~450 nm) and LC absorbance (centered ~292 nm) decrease in intensity with longer exposure time as well as a new absorbance forming at ~400 nm. These observations indicate that there is some photodegradation of the Ru(II) species and a new Ru-species is forming. The pyrene absorbances between ~300-375 nm appear to be nearly unchanged during the light exposure.

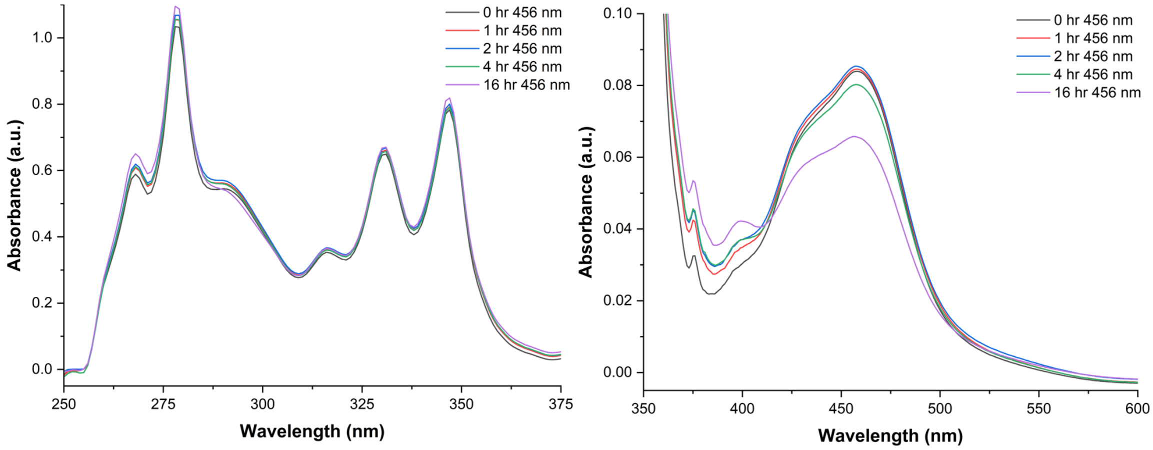


Figure S21. Relative UV/Vis spectra during the photodecomposition of poly[Ru(bpy)$_2$(dmbpy)(PF$_6$)$_2$-co-pyrene-co-MMA] dissolved under reaction conditions in DMSO under nitrogen without the presence of substrate, trapping agent, or DIPEA and exposed to 456 nm LEDs over 16 hours with stirring. The MLCT absorbances of the Ru(II) species (centered ~450 nm) decrease in intensity with longer exposure time as well as a new absorbance forming at ~400 nm. These observations indicate that there is some photodegradation of the Ru(II) species and a new Ru-species is forming. The pyrene absorbances between ~300-375 nm appear to be nearly unchanged during the light exposure.

We observe photodegradation of the Ru(II) species in both poly[Ru(bpy)$_2$(dmbpy)(PF$_6$)$_2$-co-pyrene-co-MMA] and small molecule Ru(bpy)$_2$(dmbpy)(PF$_6$)$_2$ during the exposure of these species to 456 nm in DMSO. This may, in part, explain why the yield of the reaction plateaus after a certain time point for both catalysts, based on less active catalyst over time. In addition, it appears that the Ru(II) species in the poly[Ru(bpy)$_2$(dmbpy)(PF$_6$)$_2$-co-pyrene-co-MMA] copolymer may be more photostable under the same conditions as the relative decrease in intensity of the MLCT absorbances decrease at a slower rate than that of Ru(bpy)$_2$(dmbpy)(PF$_6$)$_2$. This affect may be due to the aggregation of the copolymer chains which may slow the degradation pathway. The presence of the new band at ~400 nm with longer exposure times appears to primarily occur with only the poly[Ru(bpy)$_2$(dmbpy)(PF$_6$)$_2$-co-pyrene-co-MMA] copolymer and does not exist to a great extent in the small molecule Ru(bpy)$_2$(dmbpy)(PF$_6$)$_2$ system. This species does share some resemblance to the UV/Vis spectra of Ru(bpy)$_2$(DMSO)$_2$(PF$_6$)$_2$ and may be a result of a bipyridine ligand dissociating and DMSO ligands forming.[8]

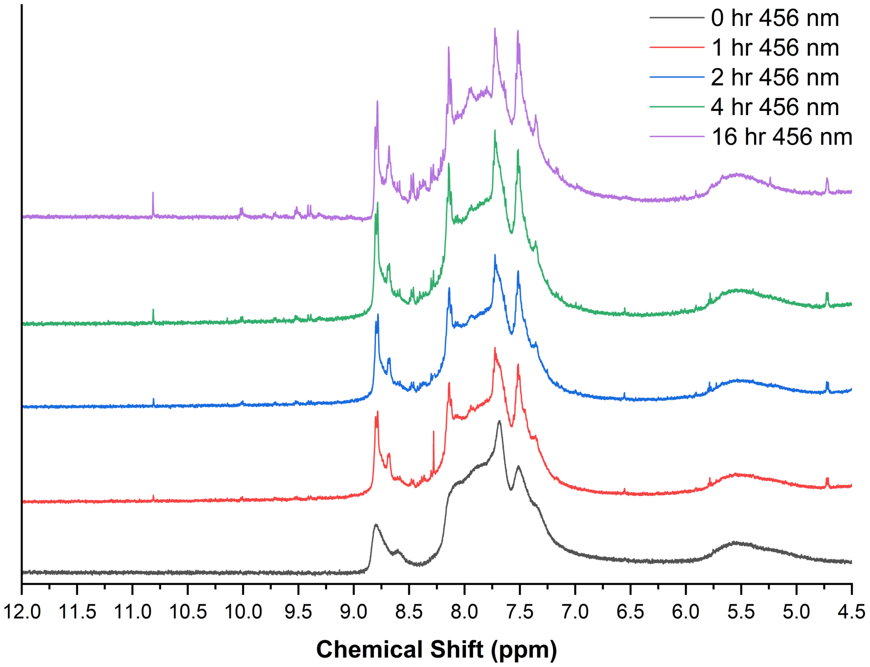


Figure S22. ^{1}H-NMR spectra during the photodecomposition of poly[Ru(bpy)$_2$(dmbpy)(PF$_6$)$_2$-co-pyrene-co-MMA] dissolved at reaction concentrations in DMSO under nitrogen without the presence of substrate, trapping agent, or DIPEA and exposed to 456 nm LEDs over 16 hours with stirring. Notably, new resonances in the region of 9.0-11.0 ppm begin to form with longer exposure times, as well as new resonances between 4.5-9.0 ppm. While these new species are currently unknown, this is clear evidence that some new species are forming (likely Ru-species based on UV/Vis data).

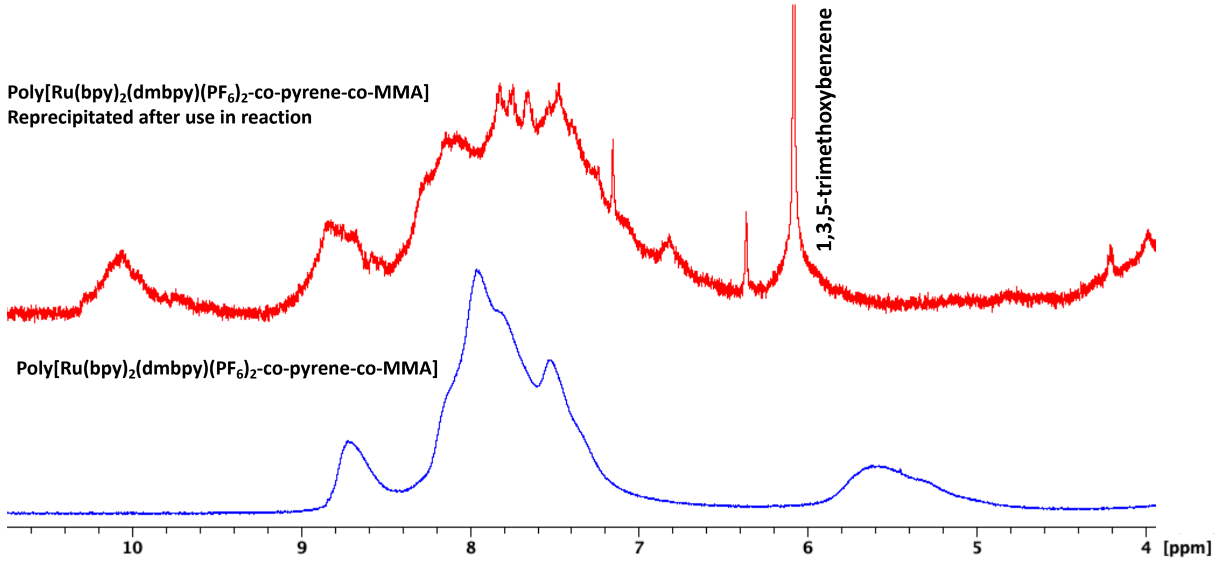


Figure S23. ^{1}H-NMR spectrum (acetone-d$_6$) of poly[Ru(bpy)$_2$(dmbpy)(PF$_6$)$_2$-co-pyrene-co-MMA] as synthesized (bottom) and reprecipitated after use as a catalyst in reaction (top) between 2-bromobenzonitrile and 1,3,5-trimethoxybenzene.

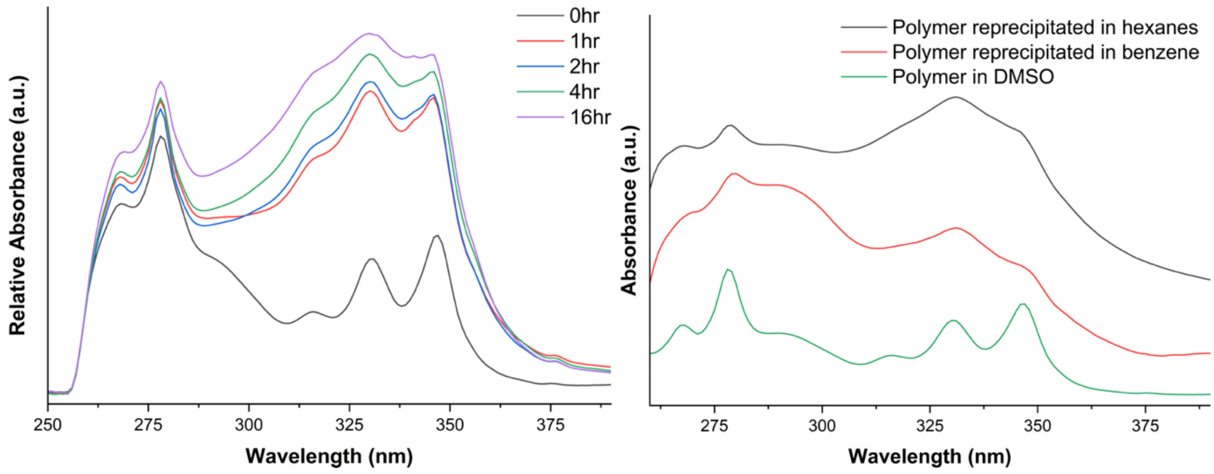
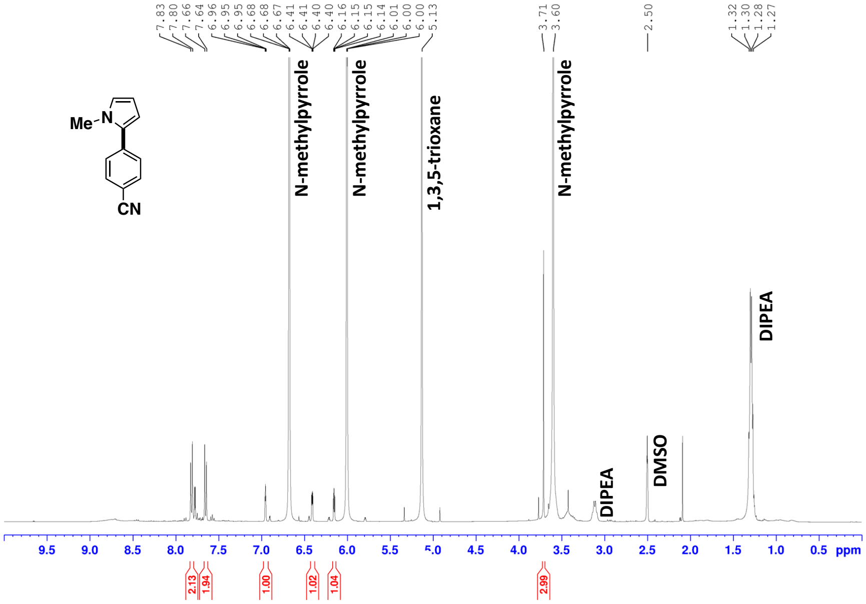


Figure S24. (Left) UV-Vis spectra of reaction mixture between 4-bromobenzontirile and N-methylpyrrole during the course of reaction (Right) UV-Vis spectra of poly[Ru(bpy)$_2$(dmbpy)(PF$_6$)$_2$-co-pyrene-co-MMA] reprecipitated in hexanes and benzene after the course of reaction between 4-bromobenzontirile and N-methylpyrrole.

8) NMR Spectra of Crude Reaction Mixtures

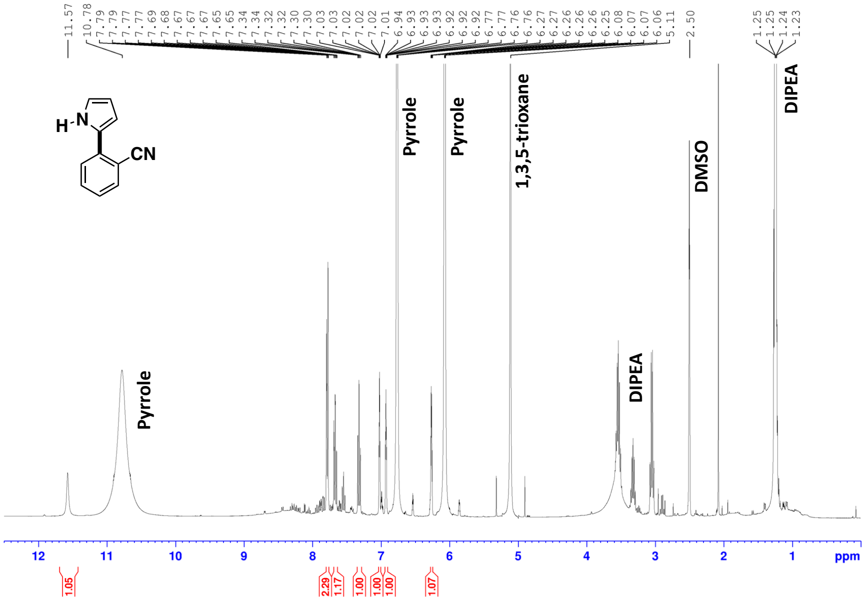
4-(1-methyl-1H-pyrrol-2-yl)benzonitrile

^{1}H NMR (400 MHz, DMSO-d$_6$): δ=7.82 (d, 2H), 7.65 (d, 2H), 6.95 (t, 1H), 6.40 (dd, 1H), 6.15 (dd, 1H), 3.71 (s, 3H) ppm



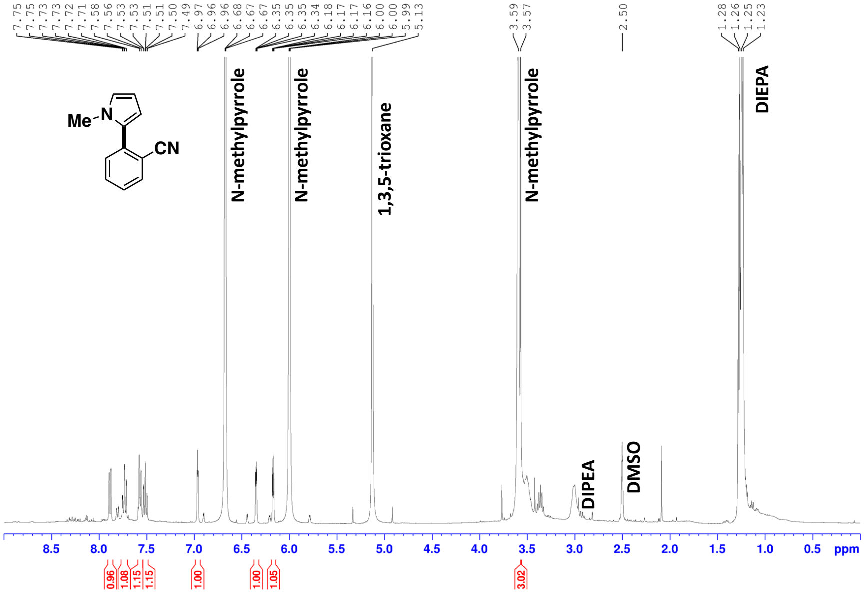
2-(1*H*-pyrrol-2-yl)benzonitrile

^{1}H NMR (400 MHz, DMSO-d$_6$): δ=11.57 (s, 1H), 7.78 (d, 2H), 7.67 (t, 1H), 7.32 (t, 1H), 7.02 (m, 1H), 6.93 (m, 1H), 6.26 (m, 1H) ppm



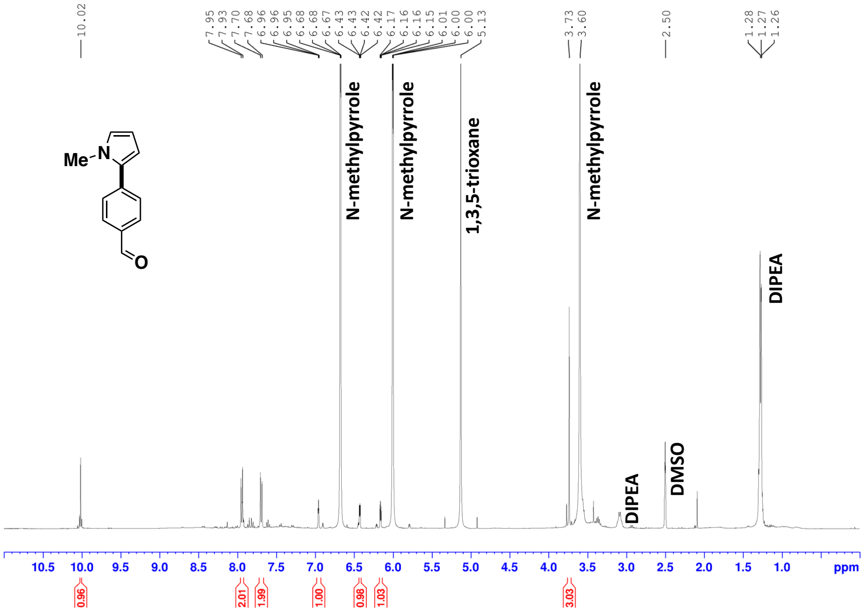
2-(1-methyl-1*H*-pyrrol-2-yl)benzonitrile

^{1}H NMR (400 MHz, DMSO-d_6): δ=7.88 (d, 1H), 7.73 (t, 1H), 7.57 (m, 1H), 7.51 (t, 1H), 6.96 (t, 1H), 6.35 (dd, 1H), 6.17 (dd, 1H), 3.57 (s, 3H) ppm



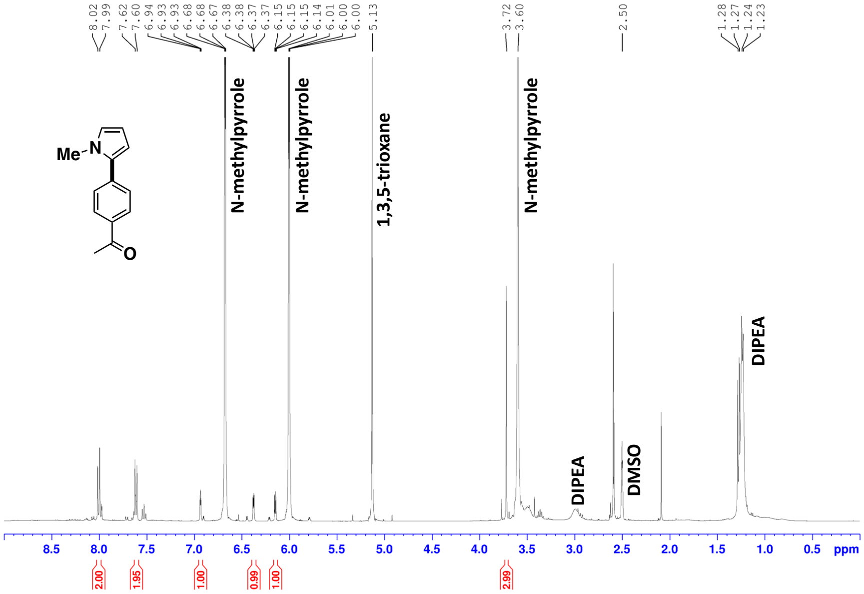
4-(1-methyl-1*H*-pyrrol-2-yl)benzaldehyde

^{1}H NMR (400 MHz, DMSO-d_6): δ=10.02 (s, 1H), 7.94 (d, 2H), 7.69 (d, 2H), 6.96 (t, 1H), 6.43 (dd, 1H), 6.16 (dd, 1H), 3.73 (s, 3H) ppm



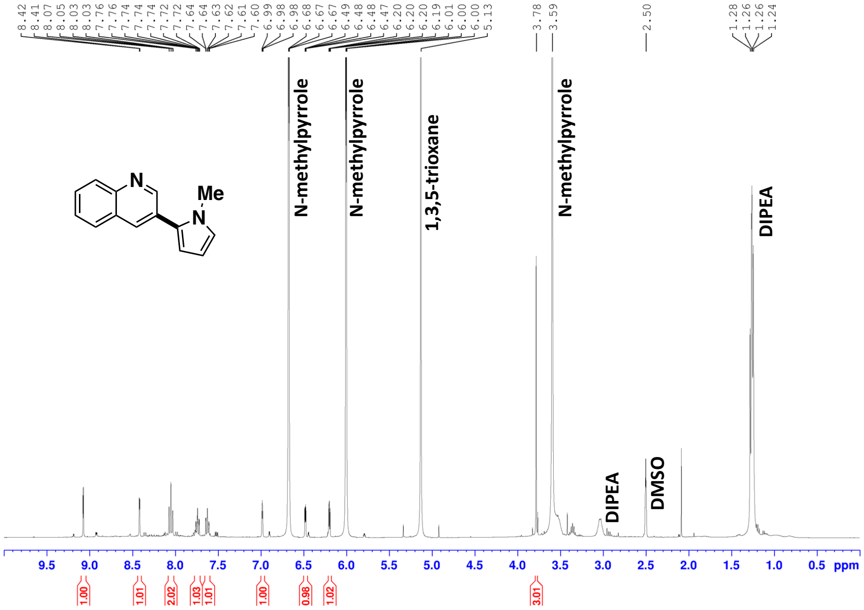
1-(4-(1-methyl-1*H*-pyrrol-2-yl)phenyl)ethan-1-one

^{1}H NMR (400 MHz, DMSO-d$_6$): δ=8.00 (d, 2H), 7.61 (d, 2H), 6.93 (t, 1H), 6.38 (dd, 1H), 6.15 (dd, 1H), 3.72 (s, 3H) ppm



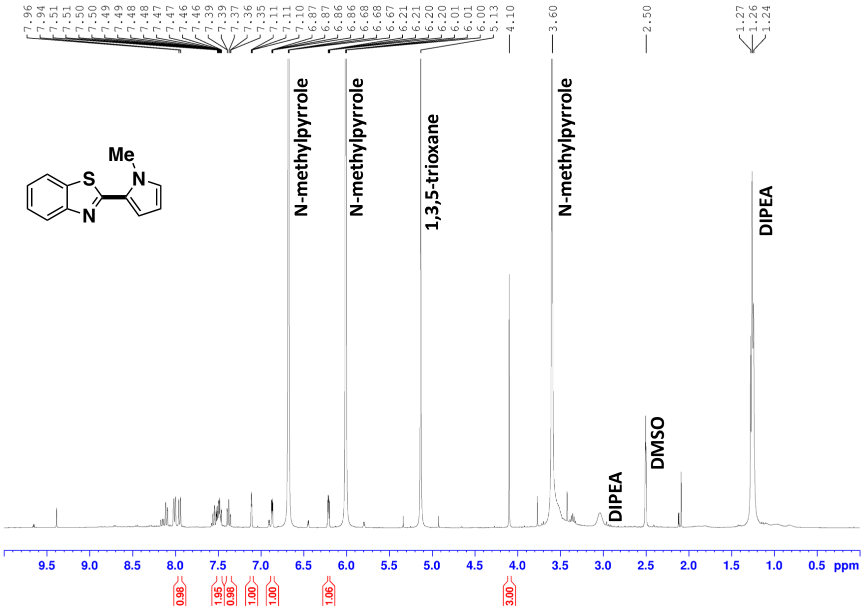
3-(1-methyl-1*H*-pyrrol-2-yl)quinoline

^{1}H NMR (400 MHz, DMSO-d$_6$): δ=9.07 (d, 1H), 8.42 (d, 1H), 8.05 (t, 2H), 7.74 (m, 1H), 7.62 (m, 1H), 6.98 (t, 1H), 6.48 (dd, 1H), 6.20 (dd, 1H), 3.78 (s, 3H) ppm



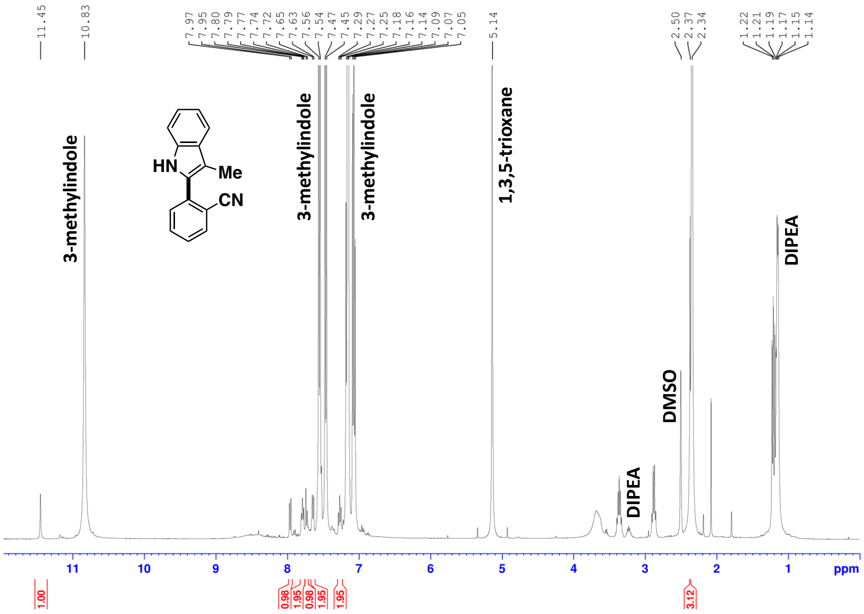
2-(1-methyl-1*H*-pyrrol-2-yl)benzo[*d*]thiazole

^{1}H NMR (400 MHz, DMSO-d$_6$): δ=7.95 (d, 1H), 7.49 (m, 2H), 7.37 (t, 1H), 7.11 (t, 1H), 6.87 (dd, 1H), 6.21 (dd, 1H), 4.10 (s, 3H) ppm



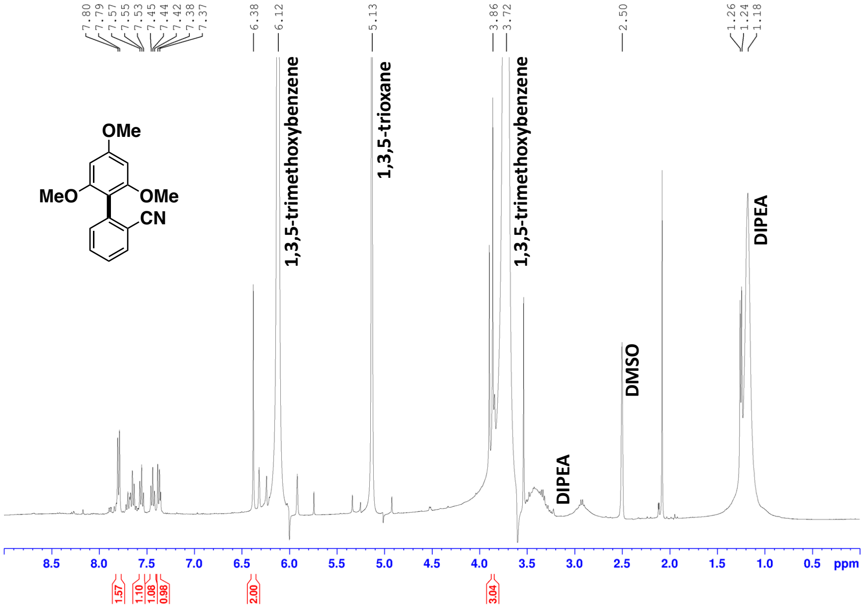
2-(3-methyl-1*H*-indol-2-yl)benzonitrile

^{1}H NMR (400 MHz, DMSO-d$_6$): δ=11.45 (s, 1H), 7.96 (d, 1H), 7.79 (t, 2H), 7.73 (m, 1H), 7.64 (m, 2H), 7.27 (m, 2H), 2.37 (s, 3H) ppm



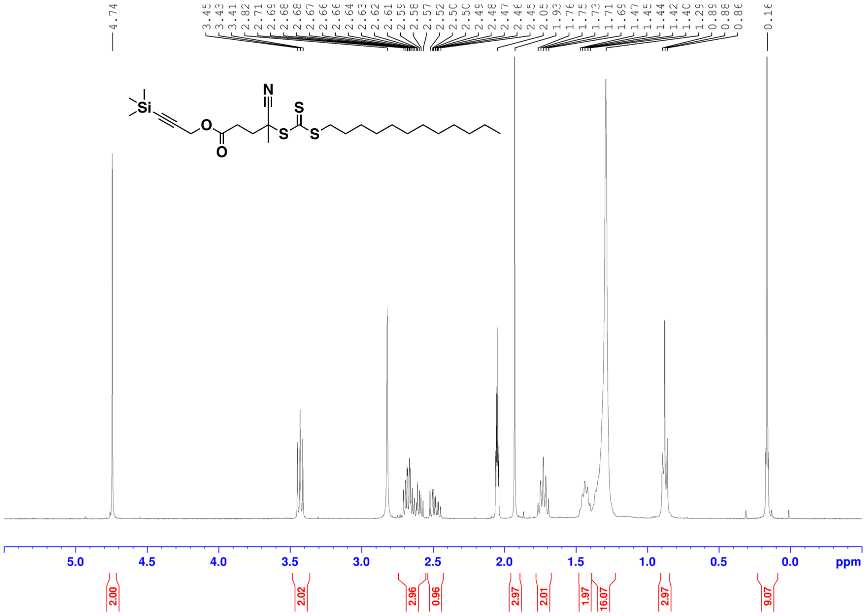
2',4',6'-trimethoxy-[1,1'-biphenyl]-2-carbonitrile

^{1}H NMR (400 MHz, DMSO-d_6): δ=7.80 (d, 1H), 7.55 (t, 1H), 7.44 (t, 1H), 7.38 (d, 1H), 6.38 (s, 2H), 3.86 (s, 3H) ppm

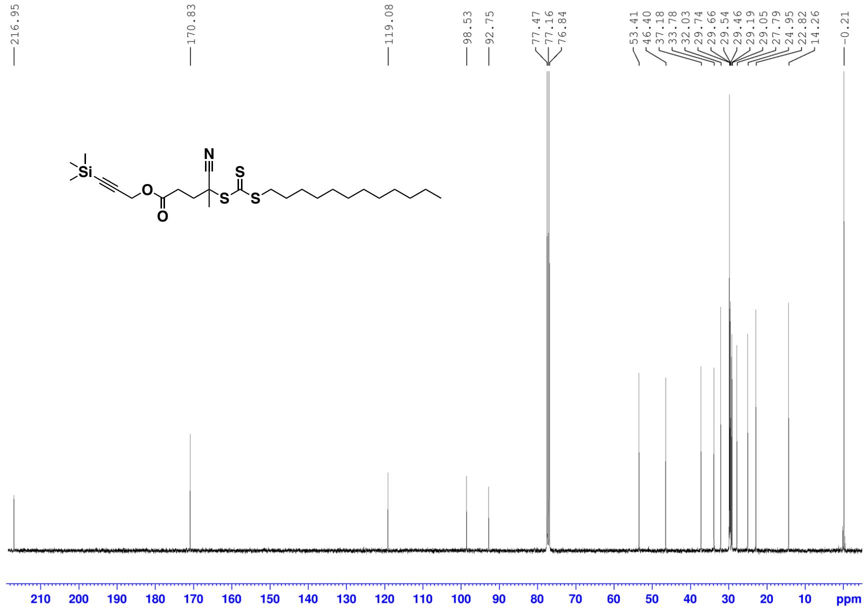


3-(trimethylsilyl)prop-2-yn-1-yl 4-cyano-4-(((dodecylthio)carbonothioyl)thio)pentanoate

^{1}H NMR (400 MHz, acetone-d_6): δ=4.74 (s, 2H), 3.43 (t, 2H), 2.63 (m, 3H), 2.48 (m, 1H), 1.93 (s, 3H), 1.73 (qu, 2H), 1.44 (m, 2H), 1.29 (m, 16H), 0.88 (t, 3H), 0.16 (s, 9H)



^{13}C NMR (100.6 MHz, $CDCl_3$): 216.95, 170.83, 119.08, 98.53, 92.75, 53.41, 46.40, 38.18, 33.78, 32.03, 29.74, 29.66, 29.54, 29.46, 29.19, 29.05, 27.79, 24.95, 22.82, 14.26, -0.21



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