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Article

Synthesis, Electrochemistry, and Photophysical Properties of a Series of Luminescent Pyrene-Thiophene Dyads and the Corresponding $Co_2(CO)_6$ Complexes

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A series of pyrene based dyad systems together with their dicobalt hexacarbonyl complexes (**1b**−**6b**) were synthesized. The pyrene-thiophene dyads are luminescent in room temperature solution with luminescence lifetimes on the nanosecond time scale. At room temperature the dyad emission is quenched by coordination to a $Co_2(CO)_6$ moiety via an acetylene bridge. However, at 77 K this emission is not fully quenched following complexation. Electrochemical studies suggest that an intraligand state is responsible for the emission. Photochemical studies in the presence of PPh_3 indicate that CO loss occurs following broadband irradiation with $\lambda_{exc} > 400$ nm, resulting in the formation of both -pentacarbonyl and -tetracarbonyl photoproducts.

Introduction

In recent years organometallic systems containing transition metals bound to highly π-conjugated systems have been the subject of extensive investigations.[1] These systems often contain pyridyl, thienyl,[2] phenyl,[2,3] and ferrocenyl[1,4] units or large polycyclic aromatic hydrocarbons (PAHs) such as pyrene,[5] perylene,[6] phenanthrene, or polypyridine ligands[7] such as 2.2′-bipyridine[8] or 1,10-phenanthroline[9] linked by alkene, alkyne, or azine type[10] bridging units. Such systems serve as models for linear molecular wires,[11] where π-conjugation extends through the length of the organic ligand.[2,7,12] The synthesis of aryl acetylene compounds using a Sonogashira−Hagihara coupling reaction is an excellent route to conjugated π-systems such as molecular wires and molecular electronic devices[13] and also facilitates incorporation of heteroaromatic rings such as thiophenes, pyridines, and large highly conjugated aromatic systems. Coupled thiophene units are known to be good electronic conductors,[14] as they enhance π-conjugation and thus π-delocalization,[13] and promote electronic coupling between terminal units.[15] Moreover, thiophene subunits can be functionalized to improve their solubility in water. They also offer the possibility of tethering to a surface via the heteroatom lone pair of electrons, and undergo electropolymerization.[16] In recent years there has been a growing interest in the use of dicobalt hexacarbonyl derivatives for the development of metallodendrimers,[17] as precursors in the catalytic Pauson−

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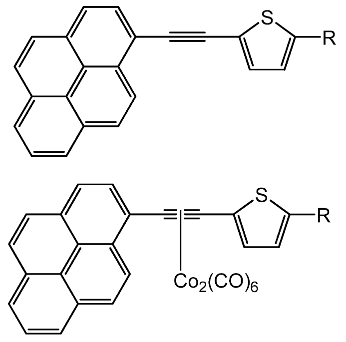
Khand reaction[18] and as redox active sensors in biological probes.[19] Much recent work has involved the generation of luminescent metal-containing alkynyl compounds.[20] Materials containing a conjugated chromophore such as pyrene or phenanthrene, and transition metals such as Ru or Pt are highly luminescent.[21] In most cases the excited-state behavior of these compounds involves ^{3}MLCT states, as the $^3\pi$-π^* charge transfer contributions are much higher in energy. This results in the frequently observed MLCT based luminescence. It has, however, been observed that by strategically placing the acetylide unit, the energy of the ^{3}IL (intraligand) state can be altered.[21,22] Castellano and co-workers have reported that the ^{3}MLCT excited state can be used as an internal sensitizer for the formation of a ^{3}IL excited state on an adjacent pyrenylacetylide ligand which results in long-lived phosphorescence.[23,24] Potential applications for such systems include luminescent probes,[21] labels for biomaterials,[25,26] DNA probes,[27] devices for artificial photosynthesis,[28,29] molecular switches and logic gates,[30] optoelectronic devices[31] such as organic field-effect transistors (OFETS) and light-emitting diodes,[31] or smart polymers.[32]

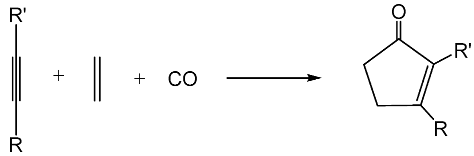
In this contribution, we describe the synthesis, characterization, electrochemistry, photophysical and photochemical properties of a series of pyrenylacetylene compounds bearing a thiophene unit and the corresponding $Co_2(CO)_6$ complexes (Chart 1). Our interest in these systems stems from the observation that such systems containing polycyclic aromatic units such as pyrene are highly fluorescent and further coupling to an extended π-conjugated system replaces the typical pyrene based emission with CT (charge transfer) based emission. These highly fluorescent systems are very sensitive to changes in the properties of the π-conjugated ligands used, with small changes resulting in notable shifts in the absorption and emission spectra, as well as metal coordination which may result in complete fluorescence quenching. As such these type of systems show great potential in the area of molecular sensors.[14] Fairlamb and co-workers[33] have also shown the viability of metal carbonyl systems as CO-releasing molecules for therapeutic use in biological systems. In addition such complexes may be employed in the synthesis of cyclopentenones via the Pauson−Khand reaction (Reaction 1),[34] where the $Co_2(CO)_6$ complexed ligand acts both as the ligand source for cyclopentenone formation and also as the cobalt catalyst. The cyclopentenone species formed may be further used in the area of natural product chemistry in the formation of prostaglandins[35] and a number of other pharmaceutically active compounds.[36]

Chart 1



R = H, Br, CHO, or $CH(CN)_2$

Reaction 1



(1)

Experimental Section

Materials. All manipulations were carried out under an atmosphere of argon or nitrogen using standard Schlenk techniques. All solvents were supplied by the Aldrich Chemical Co. Dichloromethane, chloroform, diethyl ether, pentane and cyclohexane were dried over $MgSO_4$ prior to use. Ethanol and methanol were distilled from magnesium turnings before use. Tetrahydrofuran was distilled from sodium/benzophenone ketyl solution and diisopropylamine was distilled from potassium hydroxide prior to use. All solvents used in emission and lifetime experiments were of spectroscopic grade and were used without further purification. Silica Gel (Merck) was used as received. All mobile phases for column chromatography

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were dried over $MgSO_4$ before use. 5-bromo-2-thiophene carboxaldehyde was purified by distillation using a Büchi Kügelrohr apparatus. The starting materials 1-trimethylsilylethynylpyrene and 1-ethynylpyrene were synthesized according to literature methods.[8] All other chemicals were obtained commercially and were used without further purification. All solutions were deoxygenated by purging with pure argon or nitrogen for ~10 min. Column chromatography was carried out using either neutral silica gel pH 6.5−7.5 or neutral aluminum oxide.

General Methods. IR spectra were recorded on a Perkin-Elmer 2000 FTIR spectrophotometer (2 cm^{-1} resolution) in a 0.1 mm sodium chloride liquid solution cell using spectroscopic grade pentane, cyclohexane, or dichloromethane. ^1H NMR and ^{13}C NMR were recorded on a Bruker AC 400 spectrophotometer in $CDCl_3$ or acetone-d_6 and were calibrated relative to the residual proton peaks of the solvent. All UV−vis spectra were measured in spectroscopic grade solvents on a Hewlett-Packard 8452A-photodiode-array spectrometer using a 1 cm quartz cell. Elemental analysis of C, H, and N were carried out by the Chemical services Unit, University College Dublin using an Exeter Analytical CE-440 elemental analyzer. Melting points were measured on a Gallenkamp melting point apparatus. Electrospray ionization (ESI) mass spectra were obtained using a Bruker-Esquire LC_00050 electrospray ionization at positive polarity with cap-exit voltage of 77.2 V. Spectra were recorded in the scan range 100−1000 *m/z* with an acquisition time of 300−3000 μs and a potential of 30−70 V. Recorded spectra were the summation of 10 scans. Because of poor solubility and ionization problems, mass spectrometry measurements could not be obtained for the dicobalt complexes using the available ESI instrumentation.

Steady-State Photolysis. Samples of the dicobalt hexacarbonyl complexes were dissolved in pentane solution in the presence of an excess of the trapping ligand triphenylphosphine, such that the optical density of the ν_{CO} bands were approximately 1 A.U. prior to irradiation. A small sample of this solution was placed in an IR liquid cell with a 1 mm Teflon spacer and NaCl optical windows. The solution was irradiated with broadband irradiation at 60 s intervals using a 300 W xenon-arc lamp, and spectral changes were monitored by IR spectroscopy.

Syntheses. We report the synthesis of a new series of luminescent pyrene based dyad systems containing thienyl terminal units linked by an ethynyl bridge. This synthesis was achieved by reaction of the previously synthesized 1-ethynylpyrene with the relevant brominated thienyl ligand via a palladium-catalyzed Sonogashira cross-coupling reaction. The dicyanovinyl derivatives were synthesized by a Knoevenagel condensation of the relevant aldehyde in the presence of malonitrile and piperidine. The dicobalt hexacarbonyl complexes of these compounds were synthesized by reaction of the ethynylated ligand with dicobalt octacarbonyl under mild conditions. These compounds were characterized by FT-IR, UV−vis, ^1H and ^{13}C spectroscopy, mass spectrometry, and elemental analysis.

General Procedure for Preparation of Pyrene-Thiophene Dyads via a Sonogashira Cross-Coupling Reaction. To freshly distilled and argon purged diisopropylamine ((*i*-Pr_2)NH) was added the appropriate substituted ethynylpyrene ligand, followed by catalytic quantities of $PdCl_2(PPh_3)_2$, copper(I) iodide, and triphenylphosphine. This solution was then purged with argon for a further 5 min, and the brominated ligand added. The solution was stirred overnight and subsequently heated to reflux temperature under inert conditions. In certain cases stirring alone at room temperature was sufficient for reaction to occur. Solvent was then removed under reduced pressure. The resulting residue was purified by column chromatography on silica gel with a suitable mobile phase. Solvent was removed by rotary evaporation yielding the desired compound.

2-Pyrenylacetylene-thiophene (3a). To diisopropylamine (25 mL) was added 1-ethynylpyrene (0.200 g, 0.88 mmol), $PdCl_2(PPh_3)_2$ (0.037 g, 0.053 mmol, 6%), CuI (0.010 g, 0.053 mmol, 6%), PPh_3 (0.028 g, 0.106 mmol, 12%) and 2-bromothiophene (0.085 mL, 0.88 mmol). This solution was then allowed to stir overnight under inert conditions and subsequently heated to reflux for 5 h to yield a bright yellow solution. Solvent was removed under reduced pressure. The yellow residue was purified by column chromatography on silica gel with a 4:1 petroleum ether/CH_2Cl_2 mobile phase. The desired product eluted off the column as the first intense yellow band. Solvent was removed by rotary evaporation yielding a brightly colored yellow solid. Yield: 0.240 g, 0.78 mmol, 88%; IR (CH_2Cl_2): ($\nu_{C\equiv C}$) 2199, ($\nu_{C=C}$) 1549 cm^{-1}; UV−vis (CH_2Cl_2): 236, 286, 304, 370, 396 nm; ^1H NMR (400 MHz, $CDCl_3$): 8.61 ppm (d, 1H), 8.15 ppm (m, 8H), 7.45 ppm (q, 1H, $^3J = 2.4$ Hz, $^4J = 1.2$ Hz), 7.37 ppm (q, 1H, $^3J = 4.0$ Hz, $^4J = 1.2$ Hz), 7.08 ppm (q, 1H, $^3J = 3.6$ Hz, $^4J = 1.6$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.0, 128.4, 127.4, 127.2, 126.4, 126.3, 126.2, 125.3, 124.7, 124.6, 124.4, 123.5, 116.4, 91.4, 87.2, 40.3, 28.7, 28.0, 21.6, 19.4, 13.3, 10.4; M.P. = 115−117 °C; Mass Spec. ESI *m/z* 308.1; Anal. Calcd for $C_{22}H_{12}S$, C 85.68%, H 3.92%, Found C 85.18%, H 3.96%.

2-Bromo, 5-pyrenylacetylene-thiophene (4a). To 20 mL of freshly distilled diisopropylamine was added 1-ethynylpyrene (0.400 g, 1.77 mmol), 2,5-dibromothiophene (0.199 mL, 1.77 mmol), $PdCl_2(PPh_3)_2$ (0.0742 g, 0.106 mmol), CuI (0.0201 g, 0.106 mmol), and triphenylphosphine (0.055 g, 0.212 mmol). This dark brown colored solution was then heated to reflux temperature overnight under inert conditions to yield an orange colored solution. Solvent was removed under reduced pressure, and the product purified by column chromatography on silica gel with a 80:20 petroleum ether/dichloromethane mobile phase. The desired product eluted off the column as the first bright yellow band, and solvent was removed by rotary evaporation. Yield: 0.210 g, 0.54 mmol, 30.6%; IR (CH_2Cl_2): 2194 cm^{-1}; UV−vis (CH_2Cl_2): 238, 286, 310, 378, 400, 436 nm; ^1H NMR (400 MHz, $CDCl_3$): 8.5 ppm (d,1H), 8.0 ppm (m,8H), 7.0 ppm (d, 1H, $^2J = 3.8$ Hz), 7.2 ppm (d, 1H, $^2J = 3.8$ Hz); ^{13}C NMR (100 MHz, d^6-acetone): 134.15, 132.74, 132.23, 132.05, 130.39, 130.06, 129.87, 129.59, 128.16, 127.63, 127.48, 127.34, 126.99, 125.76, 117.41, 101.01, 92.96, 87.50; M.P.: 133−135 °C; Anal. Calcd for $C_{22}H_{11}SBr$ C 68.23%, H 2.86%; Found C 68.07%, H 2.88%.

(5-(1-Pyrenylacetylene)-2-thiophene)carboxaldehyde (5a). To 20 mL of freshly distilled, argon purged diisopropylamine was added 1-ethynylpyrene (0.226 g, 1.00 mmol), $PdCl_2(PPh_3)_2$ (0.0420 g, 0.06 mmol, 6%), CuI (0.0114 g, 0.06 mmol, 6%), and triphenylphosphine (0.0314 g, 0.12 mmol, 12%) and freshly distilled 5-bromo-2-thiophenecarboxaldehyde (0.118 mL, 1.00 mmol). This solution was then stirred overnight in the dark under inert conditions to yield a bright yellow precipitate in solution. The solvent was removed under reduced pressure to yield a bright yellow solid, which was purified by column chromatography on silica gel and a 30:70 pentane/CH_2Cl_2 mobile phase. The desired product was isolated as a bright yellow-orange solid. Yield: 0.230 g, 0.68 mmol, 68%; IR ($CHCl_3$) 1672, 2197 cm^{-1}; UV−vis (CH_2Cl_2): 246, 286, 326, 352(sh.), 390(sh.), 404, 420, 372 nm;^1H NMR (400 MHz, $CDCl_3$): 9.86 ppm (s, 1H,), 8.50 ppm (d, 1H), 8.10 ppm (m, 8H), 7.69 ppm (d, 1H, $^2J = 3.9$ Hz), 7.42 ppm (d, 1H, $^2J = 3.9$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.13, 132.51, 132.10, 132.06, 131.18, 130.96, 129.67, 128.93, 128.85, 127.22, 126.48, 126.09, 126.04, 125.09, 124.61, 124.41, 124.17; M.P 120−122 °C; Mass Spec.:

ESI *m/z* 336.1; Anal. Calcd for $C_{23}H_{12}OS$: C 82.17%; H 3.59%; Found C 82.03%, H 3.60%.

(5-(1-Pyrenylacetylene)-2-thiophene)ethylene Malonitrile (6a). This dicyanovinyl derivative was synthesized via a Knoevenagel condensation reaction of the previously prepared carboxaldehyde (**5a**). To argon purged ethanol (40 mL) was added 5-(1-ethynylpyrene)-2-thiophene carboxaldehyde (0.230 g, 0.68 mmol), malonitrile (0.044 g, 0.042 mL, 0.68 mmol), and 3−4 drops of piperidine. This yellow solution was then heated to reflux temperatures for 1 h under inert conditions to yield a dark red solution. Solvent was removed under reduced pressure yielding a dark red-maroon solid. This residue was purified by column chromatography on silica gel and eluted with CH_2Cl_2. The red-orange band was collected and the solvent removed by rotary evaporation to yield the desired red product. Yield: 0.21 g, 0.55 mmol, 79%; IR (CH_2Cl_2): ($\nu_{C=C}$) 1574, ($\nu_{C\equiv N}$) 2227, ($\nu_{C\equiv C}$) 2187 cm^{-1}; UV−vis (CH_2Cl_2): 478, 396, 356, 284, 274, 240 nm; ^1H NMR (400 MHz, $CDCl_3$): 8.5 ppm (d, 1H), 8.2 ppm (m, 8H), 7.8 ppm (s, 1H), 7.7 ppm (d, 1H, $^2J = 4.0$ Hz), 7.45 ppm (d, 1H, $^2J = 4.0$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 137.5, 134.6, 131.5, 131.2, 130.86, 130.13, 129.91, 128.78, 128.18, 126.18, 125.55, 125.28, 125.22, 123.96, 123.65, 112.88, 99.62; M.P.: 120−122 °C; Mass Spec.: ESI *m/z* 384.1; Anal. Calcd for $C_{26}H_{12}N_2S$: C 81.22%; H 3.14%; N 7.28%; Found C 79.37%, H 3.33%, N 7.12%.

2-Pyrenylacetylene-5-trimethylsilylacetylene-thiophene (7a). To freshly distilled and argon purged diisopropylamine (20 mL) was added 2-ethynylpyrene-5-bromo-thiophene (0.237 g, 0.612 mmol), $PdCl_2(PPh_3)_2$ (0.514 g, 0.073 g, 6%), CuI (0.0139 g, 0.073 g, 6%), and PPh_3 (0.0385 g, 0.147 mmol, 12%). This solution was purged for a further 5 min with argon. To this solution was added trimethylsilylacetylene (0.259 mL, 0612 mmol). The solution was then heated to reflux temperatures and stirred overnight under inert conditions yielding a luminescent green-purple solution. Solvent was removed under reduced pressure to yield a dark green-brown solid. The crude product was purified by column chromatography on silica gel with a 9:1 pentane/CH_2Cl_2 mobile phase. The desired product eluted off the column as the first green colored luminescent band. Solvent was removed by rotary evaporation to yield a dark green-brown solid. Yield: 0.102 g, 0.25 mmol, 42%; IR (CH_2Cl_2): ($\nu_{c\equiv c}$) 2144, 2065 cm^{-1}, ($\nu_{c=c}$) 1644 cm^{-1}; UV−vis (CH_2Cl_2): 240, 274, 286, 310, 324, 388, 414 nm; ^1H NMR (400 MHz, $CDCl_3$): 8.55 ppm (d, 1H), 8.15 ppm (m, 8H), 7.27 ppm (d, 1H, $^2J = 4$ Hz), 7.16 ppm (d, 1H, $^2J = 4$ Hz), 0.3 ppm (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 185.93, 185.60, 130.66, 130.27, 130.09, 129.74, 128.36, 127.12, 126.80, 126.28, 125.17, 124.61, 124.40, 124.38, 70.60, 69.14; M.P.124−125 °C.

2-Pyrenylacetylene-5-acetylene-thiophene (8a). To freshly distilled and argon purged methanol (10 mL) was added 2-ethynylpyrene-5-trimethylsilylacetylene-thiophene (0.1022 g, 0.25 mmol). This was left to stir and once that the latter had dissolved, K_2CO_3 (0.0052 g, 0.0375 mmol, 15%) was added. This solution was then allowed stir at room temperature for 4−5 h. The solvent was removed under reduced pressure, and the resulting residue dissolved in 50 mL of CH_2Cl_2. This solution was then washed with 4 × 25 mL aliquots of a 5% w/v aq. $NaHCO_3$ solution. The organic fractions were combined and dried over magnesium sulfate. The combined fractions were filtered, and the solvent removed by rotary evaporation to yield a cream colored solid with near quantitative yields. Yield: 0.082 g, 0.25 mmol, 98%; IR (pentane): ($\nu_{c\equiv c}$) 2038, 2159 cm^{-1}; UV−vis (pentane): 284, 302, 316, 374, 382, and 404 nm; ^1H NMR (400 MHz, $CDCl_3$): 8.6 ppm (d, 1H), 8.2 ppm (m, 8H), 7.3 ppm (d, 1H, $^2J = 3.8$ Hz), 7.2 ppm (d, 1H, $^2J = 3.8$ Hz), 3.4 ppm (s, 1H); ^{13}C NMR (100 MHz, d^6-acetone): 141.87, 141.76, 136.83, 136.26, 134.43, 134.45, 133.39, 134.43, 13.20, 130.48, 129.92, 129.64, 129.11, 128.17, 127.65, 127.02, 125.78, 89.03, 84.96; M.P: 125−127 °C; Anal. Calcd for $C_{24}H_{12}S$ C 86.72%, H 3.64%; Found C 86.48%, H 3.66%.

General Procedure 2 for the Preparation of Dicobalt Hexacarbonyl Complexes. To a flame dried reaction flask was added pentane (10 mL), which was purged with argon for 10 min. To this solution were then added molar equivalents of the relevant substituted ethynylpyrene ligand and $Co_2(CO)_8$. This solution was stirred overnight at room temperature under inert conditions to yield a dark green-brown solution. The crude product was then subsequently purified by column chromatography on silica gel and eluted with pentane. Solvent was removed by rotary evaporation to yield a green residue.

1-Trimethylsilylethynylpyrene Dicobalt Hexacarbonyl (1b). To an argon purged pentane solution (10 mL) was added 1-trimethylsilylethynylpyrene (0.150 g, 0.50 mmol) and $Co_2(CO)_8$ (0.170 g, 0.50 mmol). This solution was then stirred overnight at room temperature under inert conditions to yield a dark green solution. The crude product was then purified by column chromatography on silica gel and eluted with pentane to yield a dark green solution. Solvent was removed to yield a green residue, which was then recrystallized from hot hexane to yield the pure product. Yield: 0.20 g, 0.34 mmol, 68% (based on PyrCCTMS). IR (pentane): 2086, 2051, 2024 cm^{-1}; UV−vis (pentane): 200, 238, 272, 284, 330, 344, 364, 384 nm; ^1H NMR (400 MHz, $CDCl_3$): 8.60 ppm (d, 1H), 8.10 ppm (m, 8H), 0.5 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.42, 133.91, 131.26, 130.83, 130.54, 130.40, 130.18, 129.95, 129.39, 129.16, 129.10, 126.32, 126.10, 125.88, 125.71, 125.25, 124.18, 124.05, 123.88, 123.75, 123.30, Anal. Calcd for $C_{27}H_{18}O_6SiCo_2$: C 55.49%, H 3.10%; Found C 55.41%, H 3.22%.

1-Ethynylpyrene Dicobalt Hexacarbonyl (2b). To a flame dried reaction flask was added 1-ethynylpyrene (0.100 g, 0.44 mmol), $Co_2(CO)_8$ (0.150 g, 0.44 mmol), and 15 mL of pentane. 5 mL of CH_2Cl_2 were also added to improve the solubility of the ligand. This solution was then stirred overnight in darkness and under inert conditions. This resulted in the formation of a dark green-brown colored solution. Solvent was removed and the dark brown residue was purified by column chromatography on silica gel with a 20:80 CH_2Cl_2/petroleum ether mobile phase. The desired product eluted off the column as the first dark brown band. Yield: 0.160 g, 0.31 mmol, 70% (based on PyrCCH); IR (pentane): 2092, 2057, 2031 cm^{-1}; UV−vis (pentane): 202, 234, 268, 386, 578 nm; ^1H NMR (400 MHz, $CDCl_3$): 8.6 ppm (s, 1H), 8.2 ppm (m, 8H), 7.0 ppm (s, 1H), 2.2 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 131.60, 131.37, 131.25, 131.12, 130.88, 128.05, 128.01, 127.50, 126.38, 125.79, 125.62, 124.83, 124.60, 124.18; Anal. Calcd for $C_{24}H_{10}O_6Co_2$: C 56.28%, H 1.97%; Found C 56.18%, H 1.98%.

2-Pyrenylacetylene-thiophene Dicobalt Hexacarbonyl (3b). To argon purged hexane (20 mL) was added 2-pyrenylacetylene (0.104 g, 0.336 mmol) and $Co_2(CO)_8$ (0.116 g, 0.336 mmol) and a few drops of CH_2Cl_2 to improve solubility of the ligand. This solution was then stirred overnight under inert conditions and in darkness. Overnight stirring resulted in the formation of a dark green-brown colored solution. Solvent was removed by rotary evaporation to yield a dark green-brown residue. This was purified by column chromatography on silica gel with a hexane mobile phase. The desired product eluted off the column as an intense dark green-brown band, which was collected and solvent removed to yield a dark green-brown colored solid. Yield: 0.070 g, 0.11 mmol, 33% (based on compound **3a**); IR (CH_2Cl_2): 2089, 2056, 2028, 1602 cm^{-1}; UV−vis (CH_2Cl_2): 236, 286, 304, 352, 370, 396, 509 nm; ^1H NMR (400 MHz, $CDCl_3$): 8.61 ppm (d, 1 H), 8.13 ppm (m, 8H), 7.44 ppm (d, 1H, ^2J = 2.4 Hz), 7.37 ppm (d, 1H,^2J = 4.8 Hz), 7.09 ppm (t, 1H,^3J = 4.4 Hz, ^3J = 3.6); ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.22, 129.39, 128.42, 128.38, 127.82, 127.40, 127.23, 127.00, 126.98, 126.64, 126.52, 126.44, 126.32, 126.26, 126.21, 124.67, 124.63, 124.67, 124.63, 124.60, 124.43, 123.43; Mass Spec. ESI *m*/*z* 308 [$M^+ - Co_2(CO)_6$], 230.2 [$Co_2(CO)_4$], 202.2 [$Co_2(CO)_3$]; Anal. Calcd for $C_{28}H_{12}O_6SCo_2$: C 56.59%, H 2.04%; Found C 55.08%, H 2.15%.

2-Bromo,5-pyrenylacetylene-thiophene Dicobalt Hexacarbonyl (4b). To argon purged hexane (20 mL) was added 2-bromo,5-ethynylpyrene-thiophene (0.100 g, 0.258 mmol) and $Co_2(CO)_8$ (0.088 g, 0.258 mmol). This solution was then stirred overnight under inert conditions to yield a dark green-brown colored solution. Solvent was removed under reduced pressure to yield a dark green-brown residue, which was purified by column chromatography on silica gel with petroleum ether (40:60°). The desired product eluted off the column as a dark green band. Solvent was removed to give a dark green solid. Yield: 0.098 g, 0.14 mmol, 54% (based on compound **4a**); IR (CH_2Cl_2): 2090, 2057, 2030 cm^{-1}; UV−vis (Hexane): 204, 236, 284, 308, 368, 396, 578 nm; ^{1}H NMR (400 MHz, $CDCl_3$): 8.43 ppm(d, 1H, J = 8 Hz), 8.24 ppm (m, 8H), 7.18 ppm (d, 1H, J = 4.0 Hz), 7.15 ppm (d, 1H, J = 4.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): 29.71, 30.96, 120.38, 121.74, 123.73, 124.10, 124.56, 125.30, 125.77, 126.33, 127.23, 128.11, 128.43, 128.59, 129.44, 130.24, 130.99, 131.20, 131.50, 132.27; Anal. Calcd for $C_{28}H_{11}O_6SBrCo_2$: C 49.95%, H 1.65%; Found C 50.21%, H 1.47%.

(5-(1-Pyrenylacetylene)-2-thiophene)carboxaldehyde Dicobalt Hexacarbonyl (5b). To a flame dried round-bottom flask was added [5-(1-ethynylpyrene)-2-thienyl]carboxaldyde (0.100 g, 0.297 mmol) and $Co_2(CO)_8$ (0.111 g, 0.326 mmol). To this was added pentane (20 mL) and 4−5 drops CH_2Cl_2 to improve the solubility of the aldehyde. This solution was then stirred overnight in darkness and under inert conditions. This resulted in the formation of a dark green solution. Solvent was removed by rotary evaporation to yield a dark green solid. This was purified by column chromatography on silica gel with a 70:30 CH_2Cl_2/pentane mobile phase and the solvent removed to give a dark green crystalline solid. Yield: 0.152 g, 0.24 mmol, 83% (based on 5a); IR (CH_2Cl_2): 2093, 2060, 2033, 1664 cm^{-1}; UV−vis (CH_2Cl_2): 236, 282, 366, 390, and 602 nm; ^{1}H NMR (400 MHz, $CDCl_3$): 9.9 ppm (s, 1H), 8.3 ppm (d, 1H), 8.1 ppm (8H, m), 7.7 ppm (d, 1H, ^2J = 3.9 Hz), 7.2 ppm (s, 1H, ^2J = 3.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): 182.80, 182.55, 182.49, 175.35, 143.49, 137.31, 133.46, 132.89, 131.69, 130.73, 128.30, 126.54, 125.99, 125.87, 125.62, 119.95, 118.94, 108.67; Anal. Calcd for $C_{29}H_{12}O_7SCo_2$: C 55.97%, H 1.94%; Found C 55.65%, H 1.20%.

(5-(1-Pyrenylacetylene)-2-thiophene)ethylene Malonitrile Dicobalt Hexacarbonyl (6b). To 20 mL of pentane was added 5-(1-ethynylpyrene)-2-thienyl]methylene malonitrile (0.100 g, 0.26 mmol), dicobalt octacarbonyl (0.097 g, 0.0286 mmol, 10% excess), and a few drops of CH_2Cl_2 to improve solubility. This solution was then stirred overnight at room temperature under inert conditions to yield a dark green colored solution. Solvent was removed and the resulting green-brown residue purified by column chromatography on silica gel with a 40:60 CH_2Cl_2/pentane mobile phase. The second dark green band due to the desired product was collected and the solvent removed to give a dark green solid. Yield: 0.107 g, 0.16 mmol, 62% (based on 6a); IR (CH_2Cl_2): (ν_{CO}) 2093, 2062, 2035, (ν_{CN}) 2226, ($\nu_{C=C}$) 1569 cm^{-1}; UV−vis (CH_2Cl_2): 236, 276, 286, 350, 368, 386, 590 nm; ^{1}H NMR (400 MHz, $CDCl_3$): 8.30 ppm (d, 1H), 8.20 ppm (m, 8H), 7.75 ppm (s, 1H), 7.75 ppm (d, 1H, ^2J = 4.0 Hz), 7.30 ppm (d, 1H, ^2J = 4.0 Hz); ^{13}C NMR (100 MHz, d^6-acetone) δ 172.3, 171.7, 166.6, 162.1, 158.4, 157.6, 157.1, 152.3, 151.6, 142.0, 140.8, 131.4, 130.8, 129.2, 128.4, 127.7, 127.0, 126.9, 126.7, 125.8, 119.9, 111.6, 109.6, 108.9, 104.6, 100.5, 100.0, 95.4, 55.1; Anal. Calcd for $C_{32}H_{12}N_2O_6SCo_2$: C 57.33%; H1.80%; N 4.17%; Found C 57.03%, H 1.85%, N 4.18%.

Photophysical Measurements. Emission spectra (accuracy ± 5 nm) were recorded at 298 K using a LS50B luminescence spectrophotometer, equipped with a red sensitive Hamamatsu R928 PMT detector, interfaced with an Elonex PC466 employing Perkin-Elmer FL WinLab custom built software. Luminescence lifetime measurements were obtained using an Edinburgh Analytical Instruments (EAI) Time-Correlated Single-Photon Counting apparatus (TCSPC) as described by Browne et al.[37] Emission lifetimes were calculated using a single exponential fitting function, involving a Levenberg−Marquardt algorithm with iterative reconvolution (Edinburgh Instruments F900 software) and are ±10%. The χ^2 and residual plots were used to judge the quality of the fits.

Electrochemistry Measurements. Cyclic voltammetry experiments were carried out using a CH instruments Model 600a electrochemical workstation at a scan rate of 0.1 V s^{-1}. Electrochemical studies were conducted using a three-electrode system with a 0.1 M solution of $TBAPF_6$ in anhydrous acetonitrile as the supporting electrolyte. The working electrode was either a 3 mm diameter Teflon shrouded glassy carbon or platinum electrode, which was polished before each use. The counter electrode was a platinum wire, and the reference electrode was a nonaqueous Ag/Ag$^+$ electrode. Deoxygenation of the solutions was achieved by bubbling through with argon for approximately 10 min, and a blanket of argon was maintained over the solution during all experiments. The filling solution for the nonaqueous Ag/Ag$^+$ reference electrode was 0.1 M $TBAPF_6$ and 0.1 mM $AgNO_3$ in anhydrous acetonitrile. All potentials are quoted with respect to the potentials of the ferrocene/ferrocenium couple ($E^{0'} = 0.31$ V vs Ag/Ag$^+$).

Results and Discussion

The structures of the pyrene-thiophene dyads and the corresponding complexes synthesized in this study are presented in Scheme 1. The ligands were prepared using a Sonogashira cross-coupling reaction with 1-ethynylpyrene in each case providing the pyrenyl group. 1-Ethynylpyrene (**2a**) was initially prepared from 1-bromopyrene via a trimethylsilyl protected derivative.[8] The dicobalt hexacarbonyl ($Co_2(CO)_6$) substituted complexes were prepared by stirring the appropriate ligand and $Co_2(CO)_8$ in pentane at room temperature overnight under inert conditions. In the case of compounds **5a** and **6a** dichloromethane was added to improve the solubility of the ligand. The Sonogashira cross coupling reactions were catalyzed by $PdCl_2(PPh_3)$ (6 mol %), copper (I) iodide (6 mol %), and triphenylphosphine (6 mol %) in the presence of *i*-Pr_2NH to remove the nascent acid formed (Scheme 2).

UV−vis Absorption. Electronic absorption data for the compounds and complexes in this study are summarized in Table 1. The absorption spectra for compounds **5a**, **5b**, and **6a** in CH_2Cl_2 are presented in Figure 1. The pyrenylacetylene chromophores in each case are responsible for the high energy $\pi \rightarrow \pi^*$ transitions, observed in the range 320−400

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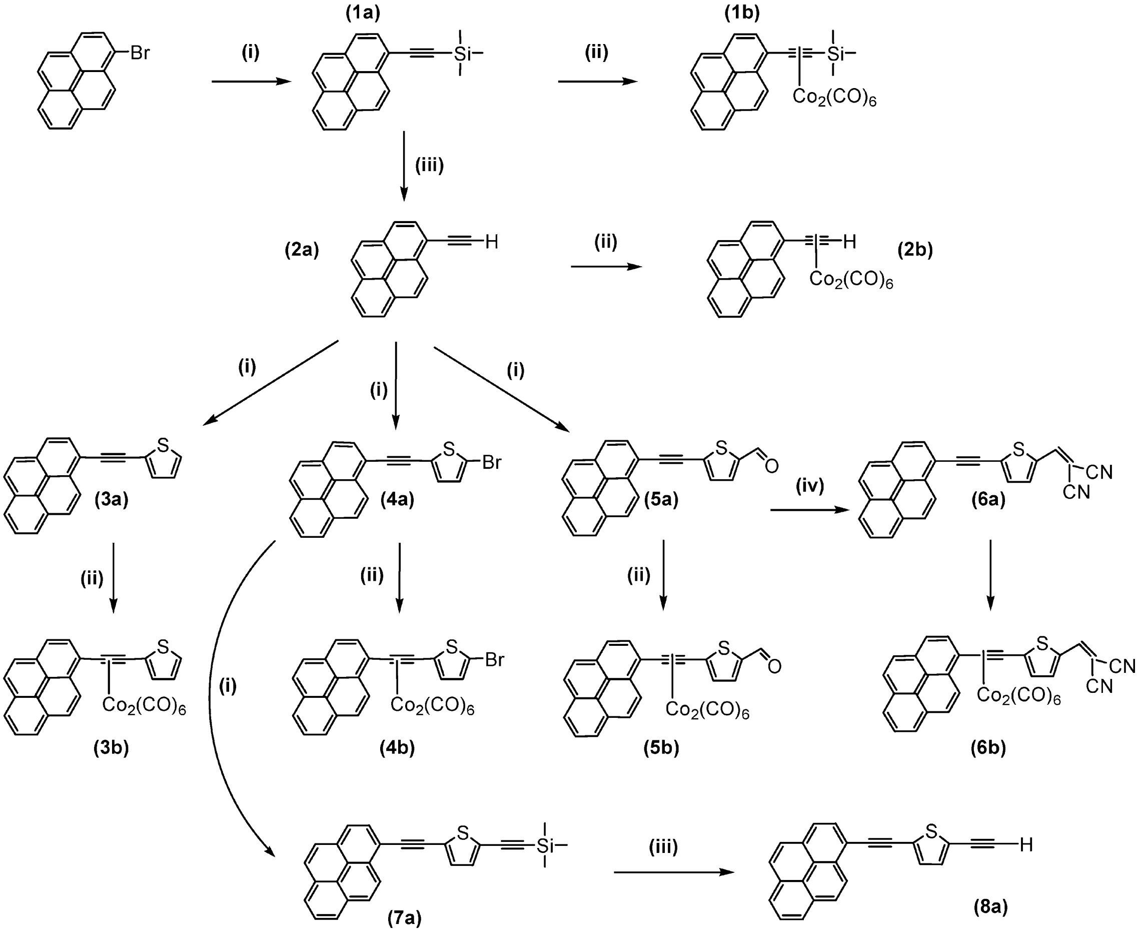
(37) Browne, W. R.; O'Connor, C. R.; Villani, C.; Vos, J. G. *Inorg. Chem.* **2001**, *40*, 5461–5464.

Scheme 1. Overview of the compounds synthesised in this study: (i) pyrene ligand, (*i*-Pr$_2$)NH, PdCl$_2$(PPh$_3$)$_2$, CuI, PPh$_3$ (6, 6, and 12 mol %); (ii) *n*-Pentane, Co$_2$(CO)$_8$; (iii) MeOH, K$_2$CO$_3$, CH$_2$Cl$_2$, 5% w/v NaHCO$_3$ (aq.); (iv)EtOH, malonitrile, piperidine, 60 °C, 1 h



nm.[38] The broad low energy band evident in compound **6a** at 478 nm is attributed to an intramolecular charge transfer (ICT) transition from the pyrenylacetylene-thienyl moiety to the electron accepting dicyanovinyl unit.[32] Coordination to Co$_2$(CO)$_6$ (compounds **1b**−**6b**) results in broader, less well-defined spectra with additional weak d-d bands between 580−600 nm, which extend to approximately 700 nm.[17,39,40] In compound **6b**, the presence of the Co$_2$(CO)$_6$ unit reduces the λ_{max} of the ICT transition to approximately 380 nm, and this band overlaps the weak ligand based $\pi \rightarrow \pi^*$ transition. For both the thiophene and bromothiophene systems (**3a** and **4a**, respectively), no noticeable shift in the λ_{max} value of approximately 400 nm assigned to $\pi \rightarrow \pi^*$ transitions is observed following complexation with Co$_2$(CO)$_6$ (**3b** and **4b**).

Luminescence Studies. Room temperature emission studies of the ligands and complexes in this study were carried out in CH$_2$Cl$_2$ as were luminescence lifetime measurements using the SPC technique. For all organic ligands in this series, irradiation of each of the different absorption bands resulted in the same emission band. Solutions were prepared such that they were isoabsorbtive at a selected wavelength, having an optical density in solution of approximately 0.3 A.U. No shift in the band position was observed, for the cobalt complexes, when compared to the pyrene ligands, which suggests that following complexation the origin of the emission band is ligand based. As is evident in Figure 2 visible excitation led to structured luminescence for all pyrenyl-acetylide compounds in this study.

Compounds **3a**−**8a** are strongly luminescent at room temperature (298 K) in dichloromethane solution. In compounds **3a** and **4a** the emission maxima are close to the lowest-energy absorption band (see Table 1), being separated by ~500 cm^{-1}. However, in contrast the Stokes shifts observed for compounds **5a** and **6a** are significantly larger at ~3800 cm^{-1} and ~4600 cm^{-1}, respectively. This may be as a result of the destabilizing effect of the more electronegative aldehyde and dicyanovinyl terminal units.[41] Compound **3a** exhibits two emission bands centered at 404 and 425 nm. The emission bands of the bromothiophene analogue (**4a**) are red-shifted to 410 and 430 nm, respectively. As shown in Figure 2, both **5a** and **6a** exhibit a single broad, intense emission band at 503 and 612 nm, respectively. This red-shift of ~3550 cm^{-1} in the emission maximum, observed

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(38) Kozlov, D. V.; Tyson, D. S.; Goze, C.; Ziessel, R.; Castellano, F. N. *Inorg. Chem.* **2004**, *43* (19), 6083–6092.

(39) Diederich, F.; Rubin, Y.; Chapman, O. L.; Goroff, N. S. *Helv. Chim. Acta* **1994**, *77*, 1441.

(40) Low, P. J.; Rousseau, R.; Lam, P.; Udachin, K. A.; Enright, G. D.; Tse, J. S.; Wayner, D. D. M.; Carty, A. J. *Organometallics* **1999**, *18*, 3885–3897.

(41) Raposo, M. M. M.; Sousa, A. M. R. C.; Kirdch, G.; Cardoso, P.; Belsley, M.; de Matos Gomes, E.; Fonseca, A. M. C. *Org. Lett.,* **2006**, *8* (17), 3681–3684.

Scheme 2. Structures of Triphenylphosphine Derivatized Photoproducts Formed, Following Steady State Photolysis with $\lambda_{exc.} > 520$ nm and $\lambda_{exc.} > 400$ nm

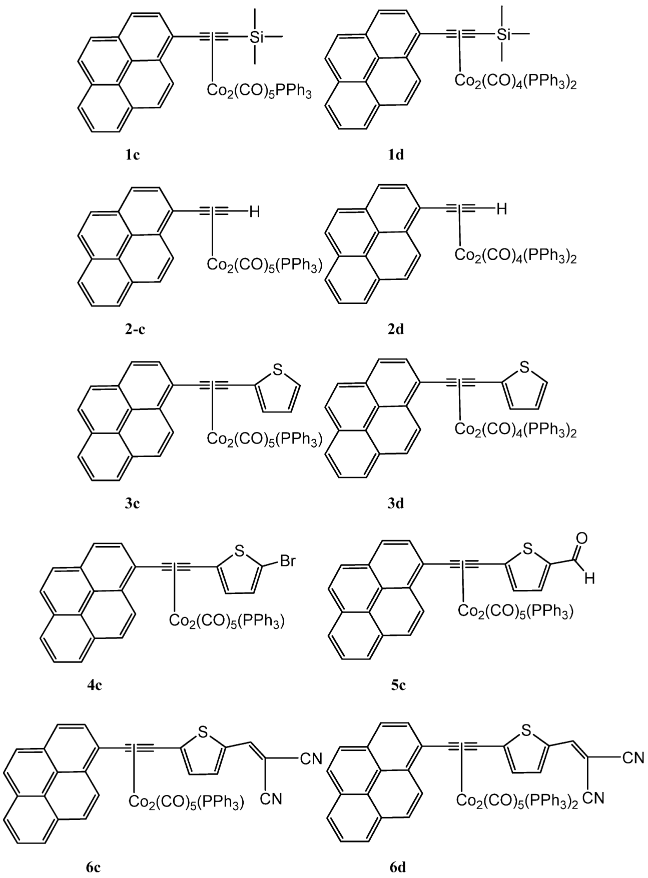

Table 1. Absorption Properties and Extinction Coefficients (ε) for the Compounds in This Study

compound	λ_{max} (nm), ε ($\times 10^7$ M^{-1} cm^{-1})
1a	272 (2.50), 284 (1.60), 330 (1.86), 344 (2.99), 364 (1.30), 384 (2.03)[a]
1b	272 (2.94)[b] 284 (2.77)[b], 330 (1.34)[b], 344(1.64)[b], 364 (1.90)[b], 388 (2.41)[b], 580 (1.02)[a]
2a	272 (2.30), 284 (1.04), 314 (7.11)[a], 328 (1.84), 342 (2.11), 360 (1.31), 384 (3.75)[a]
2b	236 (4.93), 268 (3.16), 386 (3.06), 580 (2.35)[a]
3a	286 (3.13), 304 (2.70), 370 (3.24), 396 (2.15)
3b	286 (4.64)[b], 304 (4.01)[b], 352 (4.29)[b], 370(3.92)[b], 396 (2.60)[b], 580
4a	286 (3.39), 310 (2.97), 378 (4.06), 400 (3.06)
4b	286 (3.44)[b], 310 (2.42)[b], 354 (2.49)[b], 378 (3.33)[b], 402 (3.31)[b], 580 (7.33)[a]
5a	286 (3.04), 326 (3.11), 352 (2.33), 372 (3.46), 390 (3.92), 402 (3.88), 420 (3.59)
5b	280 (3.82), 360 (2.23), 388 (2.42), 580 (1.69)[a]
6a	274 (1.88), 284 (2.07), 294 (1.26), 356 (3.37), 396 (1.93), 478 (2.92)
6b	276 (4.95), 282 (5.04), 350 (3.33), 368 (3.81), 386 (4.35), 590 (3.06)[a]
7a	274, 286, 310, 324, 388, 414
8a	274 (8.07)[a], 286 (1.13), 306 (8.07)[a], 318 (1.20), 379 (2.03), 388 (1.56), 410 (1.54)

[a] $\varepsilon = 1 \times 10^6$ M^{-1} cm^{-1}. [b] $\varepsilon = 1 \times 10^8$ M^{-1} cm^{-1}.

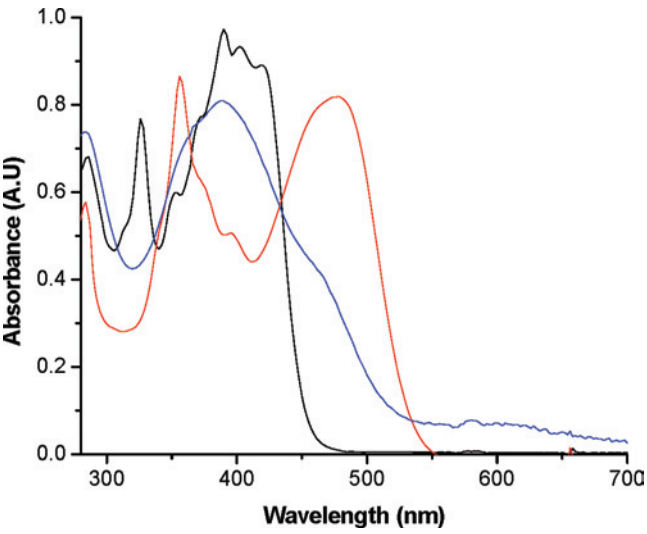

Figure 1. Overlay of the electronic absorption spectra of **5a** (black line), **5b** (blue line), and **6a** (red line) in CH_2Cl_2.

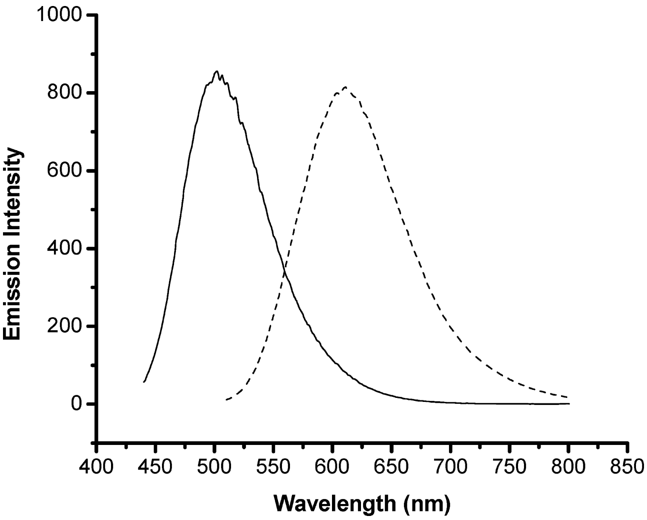

Figure 2. Room temperature emission spectra of compounds **5a** (solid line) (7.65×10^{-9} mol L^{-1}) and **6a** (dashed line) (1.03×10^{-8} mol L^{-1}) in CH_2Cl_2 solution.

on altering the terminal end, is attributed to the improved electron-accepting ability of the dicyanovinyl unit. The emission lifetimes were measured as 0.16, 0.64, 0.88, and 1.16 ns, for compounds **3a**, **4a**, **5a**, and **6a**, respectively. These values are similar to emission lifetimes previously observed for thiophene-pyrene systems.[13,14] One possibility for the increase in lifetimes observed in this study is the increase in electron delocalization within the molecule, on replacing H (**3a**), by electron accepting groups such Br (**4a**), CHO (**5a**), and $CH(CN)_2$ (**6a**).

As is evident in Figure 3, following coordination with $Co_2(CO)_6$, (complexes **3b**, **4b**, **5b**, and **6b**), a large reduction in emission intensity (up to 95%) is observed. However, no shift in the position of the emission band is obvious, thereby suggesting, that in complexes **3b**−**6b**, the observed emission is ligand based without significant MLCT contribution. The emission lifetimes obtained for the dicobalt complexes (**3b**, **4b**, **5b**, **6b)** are similar to those discussed above for the uncomplexed pyrenyl ligands. The excitation spectra of compounds **3a**−**8a** have the same shape as the corresponding absorption spectra in the range 280−400 nm, further suggesting that the emissive excited state is centered on the ligand. The excitation spectra of **6a** (Figure 4) also has the same shape as the corresponding electronic absorption spectrum for this compound in the range 280−550 nm,

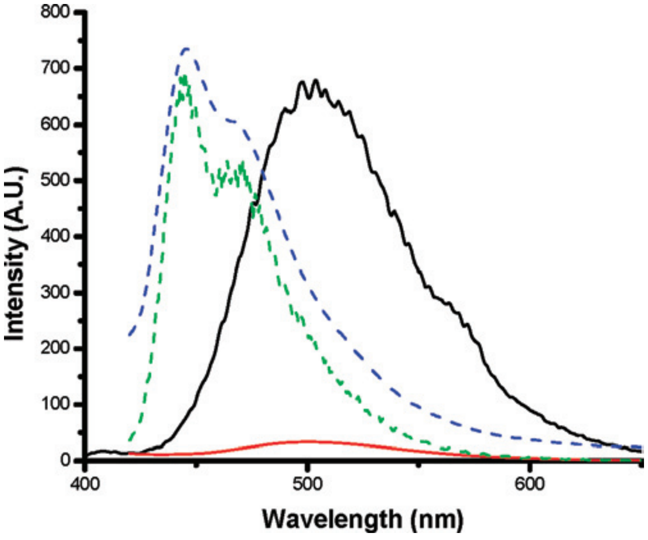

Figure 3. Room temperature (298 K) emission spectra of compounds **5a** and **5b** in CH_2Cl_2. The emission spectra of the uncomplexed aldehyde (**5a**) is represented by (black solid line) while that of the $Co_2(CO)_6$ complexed analogue (**5b**) is similarly indicated by (red solid line). Also shown are the analogous 77 K emission spectra for both **5a** (green dashed line) and **5b** (blue dashed line) in 4:1 EtOH:MeOH.

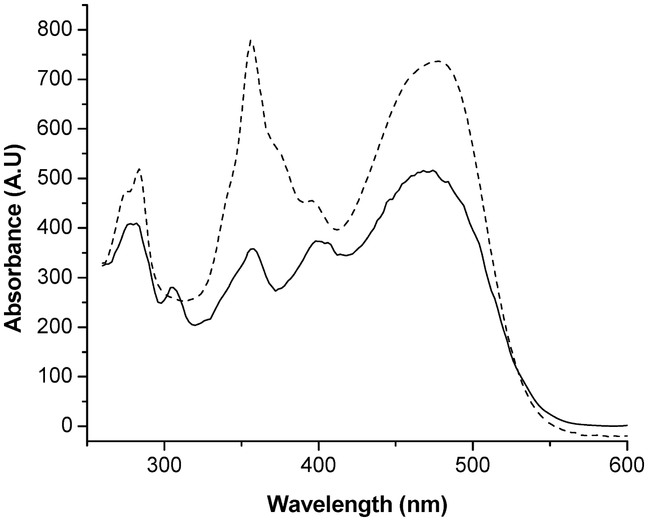

Figure 4. Overlay of excitation spectrum (solid line) and electronic absorption spectrum (dashed line) of the dicyanovinyl derivative, **6a**, in CH_2Cl_2 solution at 298 K.

thereby further confirming that the emissive excited state originates from the ligand.

Low temperature (77 K) emission studies were also undertaken in 4:1 EtOH/MeOH glasses (Table 2). At 77 K no change in the emission band position of compounds **3a** and **4a** is observed while the emission band of compound **5a** is blue-shifted by 2650 cm^{-1} to 444 nm (Figure 3). The emission band of compound **6a** is blue-shifted by ~2890 cm^{-1} at 77 K. In all four cases, as observed in the room temperature studies, complexation does not result in the generation of new emission bands. This again suggests a ligand based lowest lying excited state for the compounds in this series. This is in agreement with a number of studies[15−17] in which the emissive excited state of pyrenylacetylene bearing compounds are assigned as being predominantly IL charge transfer in nature.

Table 2. Luminescence Properties (298 and 77 K) of the Ligands and the Complexes[c]

	298 K[a]		77 K[b]	
compound	λ_{em} (nm)	τ (ns)	λ_{em} (nm)	τ (ns)
1a	387, 406	2.1, 2.1	384, 404, 420	70.9
1b	391, 409	2.3, 2.4	384, 405	42.2,
2a	385, 405	17.0	382,393,403, 420	91.7
2b	395, 425, 540	17.9	377, 420, 482, 530	3.35
3a	404, 425	0.16	404, 425	1.77
3b	400, 424	0.14	400, 424	0.88
4a	410, 430	0.64	410, 430, 445	0.45
4b	410, 430	0.63	404, 430, 443	0.75
5a	503	0.88	444, 468	55.0
5b	503	0.23	445	0.52
6a	612	1.16	520	1.73
6b	612	0.99	516	0.96
7a	420, 440	1.1, 0.2	415, 440, 455	1.49

[a] Room temperature (298 K) luminescence spectra and excited-state lifetimes recorded in spectrophotometric grade CH_2Cl_2. [b] Spectrum recorded in hexane. [c] Low-temperature (77 K) luminescence spectra and excited-state lifetimes recorded in 4:1 EtOH:MeOH.

Emission quenching has previously been reported for a few examples of metal carbonyl complexed fluorescent organic compounds. These include $[Co_2(CO)_6(\mu\text{-}\eta^2\text{-}RCH_2CCH)]$, $[Fe_2(CO)_6(\mu\text{-}S\mathit{t}Bu)(\mu\text{-}\eta^2\text{-}RCH_2C{=}CH_2)]$, $[Ru_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}RCH_2CCH)]$, and $[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}RCH_2CCH)]$, where R are the highly fluorescent acridone or 5-(dimethylamino)naphthalene-1-sulfonyl (dansyl) luminophores.[42] The fluorescence quantum yields for the complexes are 1 to 2 orders of magnitude less than either the acridone or dansyl fluorophores. Ruthenium(II) polypyridyl complexes anchored with $[Co_2(CO)_4(dppm)]$ systems have also demonstrated emission quenching upon coordination of $[Co_2(CO)_4(dppm)]$.[17] Other metal carbonyl complexed pyrenyl ligands include tricarbonylrhenium complexes of *N*,*N*′-bis[(pyrenyl)pyrazolyl]alkanes where the emission is also quenched.[43] This is in contrast to the luminescent *N*,*N*′-diimine derivatives of tricarbonylrhenium.[44] In this study we have attributed quenching to energy transfer to the cobalt carbonyl center, which is in agreement with the systems previously reported.[17,42,43] Support for such a mechanism comes from quenching experiments using pyrene and $(\mu_2\text{-}C_2(C_6H_5)_2)Co_2(CO)_6$ as model compounds, which were used to construct a Stern−Volmer plot, generating a bimolecular quenching constant of 2.15×10^{10} L $mol^{-1}s^{-1}$(see Supporting Information for details).

Electrochemistry. Cyclic voltammetry studies were carried out on compounds **1a**−**8a** in a 0.1 M $TBAPF_6/CH_3CN$ electrolyte solution (Table 3). All compounds exhibited an oxidation in the range 1.0−1.1 V versus Ag/Ag^+. This is assigned to irreversible oxidation of the pyrene unit based on previous reports in the literature,[14,17] where irreversible oxidation of the pyrene unit in a pyrene-thiophene dyad was observed at 1.25 V versus Ag/AgCl. It is suggested that this process is irreversible because of the generation of a dimer cationic species by association of the oxidized pyrene with

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Table 3. Electrochemical Properties at Room Temperature

compound	$E_{p,A}$ (V) [Irr]^a	$E_{p,C}$ (V) [Irr]	$E_{1/2}{}^b$ (V) [ΔE_p (mV)]^c
1a	0.41, 0.75, 0.97	−1.95, −1.75, −1.60	
1b	0.16, 0.39, 0.51, 0.64, 0.86, 0.97	−1.95, −1.76, −1.56, −1.28, −1.16	
2a	0.649, 1.09	−0.39, −1.35	
2b	0.51, 0.64, 0.95, 1.07		−1.27 (71)
3a	0.02, 0.90	−2.11, −1.56, −1.81,	−1.21 (81)
3b	0.56, 0.92	−1.91, −1.71,	−1.20 (86)
4a	0.95, 1.07	−1.84, −1.22,	−2.08 (49)
4b	0.67, 0.95, 1.02	−1.07, −1.19, −1.88	
5a	1.02		−1.88 (98), −1.67 (56)
5b	0.56, 0.69	−1.48, −1.18, −1.09	0.99 (45), −1.86 (44), −1.66 (59)
6a	0.48, 1.03	−1.64, −1.36, −1.10 (42)	
6b	0.92, 0.71, 0.56, 0.36	−1.37	−1.14 (74)
7a	1.00	−1.06, −1.26, −1.83	

[a] Indicates an electrochemically irreversible process. [b] Indicates a fully reversible electrochemical process. [c] $E_{1/2}$ is the separation between oxidation and reduction peak in mV (V vs Ag/Ag$^+$, scan rate 0.1 V s^{-1} in a 0.1 M TBAPF$_6$/CH$_3$CN solution).

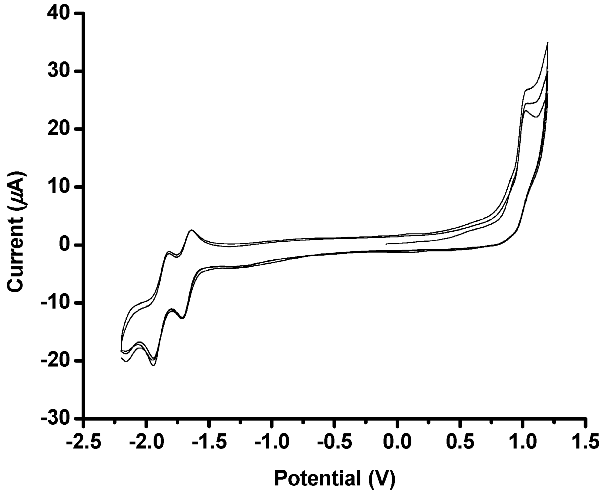

Figure 5. Cyclic voltamogramm of compound **5a** in a TBAPF$_6$/CH$_3$CN electrolyte solution.

Table 4. M-CO Band Positions in Pentane for the Parent Dicobalt Hexacarbonyl Complexes and the Photoproducts Observed in This Study

complex^a	ν_{CO} (cm^{-1} ± 2 cm^{-1})
1b	2086, 2051, 2024
1c	2059, 2012. 2001
1d	1984, 1968, 1941
2b	2092, 2057, 2030
2c	2064, 2017, 2005
2d	1979, 1971, 1947
3b	2090, 2057, 2031
3c	2064, 2021, 2007
3d	1973, 1924
4b	2091, 2058, 2033
4c	2064, 2022, 1974
5b	2093, 2060, 2033
5c	2067, 2022, 2013
5d	2001, 1975
6b	2093, 2062, 2035
6c	2067, 2025, 2014, 2001
6d	1964, 1948, 1977

[a] Parent complexes **1b**−**6b** are indicated in **bold.** Complexes labeled **c** and **d** refer to the corresponding pentacarbonyl and tetracarbonyl photoproducts, respectively.

a second pyrene subunit.[14] Oxidation at higher potentials (+1.4 V) leads to gradual loss of all characteristic oxidation and reduction potentials. This phenomenon has been previously observed[38] and has been assigned to decomposition of the complex at the electrode surface. We have however observed that in each case oxidation at high positive potentials results in "polymerization" or deposition of a film onto the working and counter electrode surfaces, which perturbs further electrochemical measurements. This explains loss of the characteristic redox processes following oxidation at high potentials. Furthermore, this may suggest that electropolymerization occurs at high positive potentials and requires further study as the electropolymerization processes in thiophene systems is known.[45] Following complexation with Co$_2$(CO)$_6$ an irreversible oxidation process is observed in each case in the range 0.55−0.70 V versus Ag/Ag$^+$. This is assigned to oxidation of the cobalt metal center and is in agreement with previous literature observations for similar systems where $E_{1/2}$(Co$^{1+/0}$) was observed in the range 0.70−0.90 V.[17,19,46]

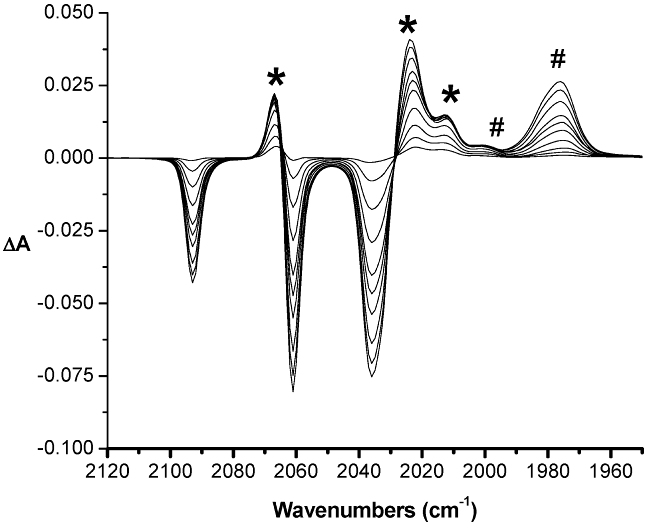

Figure 6. IR difference spectra following broadband irradiation of **5b** in pentane at λ_{exc} > 400 nm. Negative bands indicate bleaching of the parent bands while positive bands indicate formation of the pentacarbonyl (*) and tetracarbonyl species (#). Spectra obtained at 60 s intervals over total irradiation time of 10 min.

The cyclic voltammogram of compound **1a** also exhibits a quasi-reversible oxidation wave at 0.41 V and a quasi-reversible reduction wave at −1.60 V versus Ag/Ag$^+$, possessing an energy band gap (ΔEp) of 120 mV,

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while $i_{pa}/i_{pc} = 1$. This suggests that this process is a quasi-reversible one-electron process and is assigned to the reduction of the pyrene unit. However, in the case of the associated dicobalt hexacarbonyl complex (**1b**), an irreversible oxidation assigned to oxidation of the cobalt metal center is also observed at 0.511 V versus Ag/Ag^+. Complexation also shifts the quasi-reversible redox processes to lower potentials by approximately 20 mV. This indicates that coordination of the cobalt hexacarbonyl moiety reduces the reversibility of the redox system perhaps as a result of increased charge transfer from the pyrene unit to the metal center. The presence of the irreversible pyrene based oxidation is especially obvious in compound **2a**, where this oxidation is observed at 1.09 V versus Ag/Ag^+. Following complexation a broad irreversible oxidation assigned to oxidation of the cobalt metal centers is observed at 0.64 V versus Ag/Ag^+. A quasi-reversible reduction at $E_{1/2} = -1.27$ V versus Ag/Ag^+ present may be due to the reduction of the 1-ethynylpyrene unit, not previously observed for the free ligand.

The cyclic voltammogram of **3a** exhibits an irreversible oxidation at 0.90 V because of oxidation of the pyrene moiety. A quasi-reversible reductive process also observed at $E_{1/2} = -1.80$ V is assigned to the one-electron reduction of the pyrene moiety on the basis of similarities with a literature value of −1.59 V versus Ag/AgCl observed for the reduction of pyrene in an analagous system.[14] For the associated complex **3b** a cobalt based irreversible oxidation is also observed at 0.56 V versus Ag/Ag^+. The cyclic voltammogram of the bromothiophene analogue (**4a**) also exhibits an irreversible reduction process at −1.88 V assigned to the one-electron reduction of the pyrene unit, while a quasi-reversible reductive feature at −2.08 V is assigned to the one electron reduction of the thiophene unit. This low reduction potential for the thiophene unit may be attributed to the electron withdrawing effect of the appended Br. Following coordination of $Co_2(CO)_6$ (**4b**) an irreversible cobalt centered oxidation is observed at 0.67 V. Although the one-electron reduction of the pyrene unit remains at approximately −1.8 V, going from −1.84 V for **4a** to −1.88 V for the associated $Co_2(CO)_6$ complex, the band at −2.08 V previously assigned to the quasi-reversible reduction of the thiophene unit is shifted to lower reduction potentials on complexation. This lowering of the thiophene reduction potential to −1.19 V is due to increased electron donation following complexation and results in a thiophene based reduction potential, which is more in line to those observed in the literature, where the irreversible reduction of the thiophene subunit in a similar dyad system was observed at −1.40 V versus Ag/AgCl.[47]

The aldehyde derivative, **5a**, also exhibits a fully reversible one-electron reduction peak with a half-wave potential ($E_{1/2}$) of −1.67 V versus Ag/Ag^+, assigned to the reduction of the thiophene group.[47] A quasi reversible reductive process also observed at $E_{1/2} = -1.88$ V is assigned to the one-electron reduction of the pyrene moiety.[8] On complexation with $Co_2(CO)_6$ an irreversible oxidation is observed at 0.67 V versus Ag/Ag^+. Coordination of the cobalt metal center also appears to lower the reduction potential for the thiophene unit by ~500 mV to −1.18 V versus Ag/Ag^+. Furthermore, the thiophene based reduction now appears to be irreversible. As observed for **5a**, the complexed analogue **5b** also displays a quasi-reversible reduction because of reduction of the pyrene unit at a half-wave potential ($E_{1/2}$) of −1.86 V versus Ag/Ag^+. The cyclic voltammogram of ethynylpyrenethiophene carboxaldeyde (**5a**) is shown in Figure 5, however, the proximity of the reduction potentials to one another makes definite assignment difficult.

Compounds **6a** and **6b** exhibit an apparent irreversible reduction of the thiophene unit at −1.16 V and an irreversible reduction of the dicyanovinyl moiety at −1.36 V versus Ag/Ag^+. These reduction potentials are in good agreement with those observed in the range −1.37 to −1.23 V versus Ag/AgCl by Roncali and co-workers for dicyanovinyl units in triphenylamine-thienylenevinylene systems.[32]

The level of π-conjugation and thus delocalization of electron density throughout the pyrenylacetylene ligand was increased by the addition of a further ethynyl unit in the 5-position of the substituted thiophene ring resulting in the generation of compound **7a**. An apparent irreversible oxidation of the pyrene unit was observed at positive potentials of 1.00 V versus Ag/Ag^+ with no further features evident in this region. In contrast however a number of features are evident at reductive potentials. The primary reductive process involves the apparent quasi-reversible reduction of the thiophene unit at −1.26 V followed by a secondary reductive process at −1.83 V versus Ag/Ag^+ involving reduction of the pyrene unit.[8] Furthermore, a very weak reductive feature observed at −1.53 V versus Ag/Ag^+ between the thiophene and pyrene based reductions is assigned to the reduction of the ethynyl terminal unit.[8] However, because of its low intensity and proximity to two very strong reductive potentials, the assignment of this weak reductive feature must remain tentative.

Steady-State Photolysis. As presented in Table 4, extended broadband irradiation of complex **1b** with $\lambda_{exc.} > 520$ nm for 600 s in the presence of PPh_3 resulted in bleaching of the parent absorption bands together with the generation of product bands at 2059, 2012, and 2001 cm^{-1}, assigned to the pentacarbonyl species (Reaction 2). Subsequent irradiation with $\lambda_{exc} > 400$ nm for 15 min resulted in further bleaching of the parent bands and an increase in absorbance in the bands assigned to the pentacarbonyl species **1c**.[48,49] Bands were also observed under these conditions at 1984, 1968, and 1941 cm^{-1} and are assigned to the formation of the tetracarbonyl species (**1d**, Reaction 3). Similar results were obtained for complexes **2b**, **3b**, and **4b**. The assignments made in this study are based on comparisons with ν_{CO} bands for similar systems, such as $(\mu_2\text{-}C_2H_2)Co_2(CO)_5(PPh_3)$ which has stretching vibrations at 2069, 2017,

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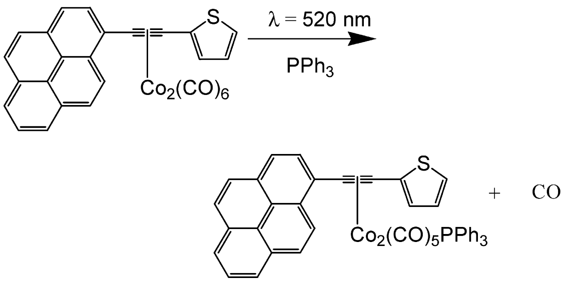
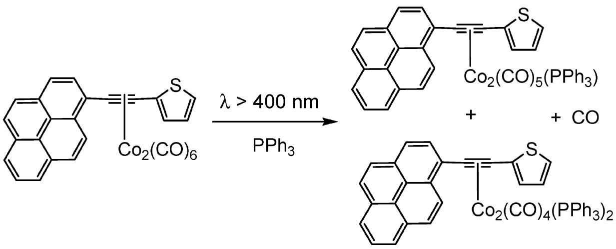
2009, 1998, 1975 cm^{-1} and, the tetracarbonyl analogue, (μ_2-C_2H_2)$Co_2(CO)_4(PPh_3)_2$ which displays ν_{CO} bands at 2028, 1982, 1965, and 1948 cm^{-1}.[50]

Reaction 2



(2)

Reaction 3



(3)

Broadband photolysis of complex **5b** with λ_{exc} > 520 nm resulted in very little change in the IR spectrum. However subsequent higher energy irradiation with $\lambda_{exc.}$ > 400 nm, resulted in the predominant formation of the pentacarbonyl species **5c** (Figure 6), with ν_{CO} bands at 2067, 2022, and 2013 cm^{-1}, with additional ν_{CO} bands at 2001 and 1975 cm^{-1} which suggest tetracarbonyl formation. Under similar conditions, broadband irradiation of complex **6b** at λ_{exc} > 400 nm resulted in bleaching of the parent absorption bands and generation of ν_{CO} bands at 2067, 2025, 2014, 2001, and 1977 cm^{-1} assigned to the pentacarbonyl species, **6c**. No evidence was obtained for formation of the tetracarbonyl photoproduct, **6d**.

Conclusion

In summary, a series of novel pyrenylacetylene compounds bearing various substituted thiophene units and their corresponding $Co_2(CO)_6$ complexes have been synthesized. The photophysical, photochemical, and electrochemical properties of these novel systems have been studied. All of the synthesized compounds absorb into the visible region, the dicyanovinyl compound **6a** absorbs further toward the red region because of an intramolecular charge transfer transition, while the presence of low energy MLCT transitions in the dicobalt complexes result in a considerable red shift in the low energy absorptions. Luminescence studies and cyclic voltammetry indicate that in all cases the lowest lying excited state is intraligand charge transfer in nature. It is suggested[32] that this charge transfer involves the formation of a pyrene$^+$−thiophene$^-$ excited state. This is further supported by electrochemical studies in acetonitrile solution. In these experiments irreversible one-electron oxidation of the pyrene unit was observed. Complexation with the $Co_2(CO)_6$ moiety has been shown to significantly quench the observed ligand based emission. This may be as a result of energy transfer from the luminescent pyrene moiety to the cobalt metal center. At low temperatures (77 K) this energy transfer process is not observed, resulting in less efficient quenching of the ligand based emission for the cobalt carbonyl complexes. Electrochemical studies also indicate that the coordinated $Co_2(CO)_6$ units are irreversibly oxidized at high oxidation potentials. Irradiation of the dicobalt carbonyl complexes in the presence of PPh_3 yields both -pentacarbonyl and -tetracarbonyl species. Low energy broadband irradiation (λ_{exc} > 520 nm) resulted in the production of the pentacarbonyl species with apparent low yield, while higher energy irradiation with λ_{exc} > 400 nm, resulted in formation of the tetracarbonyl species.

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Supporting Information Available: Figures containg UV-vis spectra and cyclic voltammograms of the compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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