Functionalization of polymers with phosphorescent iridium complexes *via* click chemistry

Supporting Information

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Materials and Methods

All reagents were purchased either from Acros Organics or Aldrich and used without further purification unless otherwise noted. THF and CH_2Cl_2 were dried via passage through copper oxide and alumina columns. ^{1}H-NMR and ^{13}C-NMR spectra (300 MHz ^{1}H NMR, 75 MHz ^{13}C NMR) were taken using a Varian Mercury Vx 300 spectrometer. All spectra are referenced to residual proton solvent. Abbreviations used include singlet (s), doublet (d), doublet of doublets (dd), triplet (t), and unresolved multiplet (m). Mass spectral analyses were provided by the Georgia Tech Mass Spectrometry Facility. Gel-permeation chromatography (GPC) analyses were carried out using a Waters 1525 binary pump coupled to a Waters 2414 refractive index detector with methylene chloride as an eluant on American Polymer Standards 10 μm particle size, linear mixed bed packing columns. The flow rate used for all the measurements was 1 mL/min. All GPC measurements were calibrated using poly(styrene) standards and carried out at room temperature. UV/vis absorption measurements were taken on a Shimadzu UV-2401 PC recording spectrophotometer. Emission measurements were acquired using a Shimadzu RF-5301 PC spectrofluorophotometer. Lifetime measurements were taken using a PTI model C-72 fluorescence laser spectrophotometer with a PTI GL-3300 nitrogen laser. Elemental analyses were obtained using a PERKIN ELMER//CHNS/O Analyzer 2400.

Experimental Procedures

Synthesis of *fac*-Bis(2-phenylbenzothiazole)-2-(4-formylphenyl)pyridine Iridium(III) (5).

A mixture of **2** (1.00 g, 0.77 mmol), 4-(2'-pyridyl)benzaldehyde (0.60 g, 3.28 mmol), $AgCF_3SO_3$ (0.42 g, 1.63 mmol), and 2-ethoxyethanol (30 mL) was purged with argon for 30 minutes at room temperature and then heated at 110 °C for 32 hours. The resulting dark orange-red solution was cooled down to room temperature and water (200 mL) was added. The precipitate was filtered, dried in the air and dissolved with 200 mL of dichloromethane. The solution was concentrated and the residue was subjected to SiO_2 chromatography using dichloromethane as the eluant. After removal of the solvent, the pure product was isolated as a red solid. Yield: 0.47 g (38%). ^{1}H NMR (300 MHz, $CDCl_3$) (ppm): δ = 6.36 (d, 1H, J = 8.1 Hz), 6.62 (t, 2H, J = 6.3 Hz), 6.75 (d, 1H, J = 8.0 Hz), 6.80-7.01 (m, 7H), 7.13 (d, 1H, J = 1.8 Hz), 7.20 (quintet, 2H, J = 8.1 Hz), 7.40 (dd, 1H, J_1 = 8.1 Hz, J_2 = 1.2 Hz), 7.67-7.71 (m, 6H), 7.95-7.98 (m, 2H), 9.97 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) (ppm): δ = 118.8, 119.1, 119.9, 120.6, 122.3, 122.5, 123.2, 123.7, 124.4, 126.2, 126.6, 127.7, 131.1, 136.4, 136.8, 149.4, 150.1, 151.3, 160.2, 165.2, 179.0, 194.0. HRMS (ESI): calculated M^+ = 795.0990; observed M^+ = 795.1044.

Synthesis of *fac*-Bis(2-phenylquinoline)-2-(4-formylphenyl)pyridine Iridium(III) (6).

The same procedure as described above for the preparation of **5** was employed. Yield: 0.44g (36%). ^{1}H NMR (300 MHz, $CDCl_3$) (ppm): δ = 6.61 (dd, 1H, J_1 = 7.8 Hz, J_2 = 1.2 Hz), 6.61 (d, 1H, J = 7.8 Hz), 6.72-6.81 (m, 3H), 6.81-6.98 (m, 4H), 7.50 (d, 2H, J = 8.1 Hz), 7.57-7.92 (m, 6H), 8.02-8.22 (m, 4H), 9.56 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) (ppm): δ = 117.8, 118.2, 120.0, 120.2, 123.1, 123.3, 125.0, 125.6, 126.0, 126.2, 126.4, 127.4, 127.5, 127.6, 127.9, 128.1, 128.8, 129.4, 129.6, 130.1, 135.8, 135.9, 136.3, 136.7, 136.9, 137.4, 138.4, 144.5, 145.9, 148.1, 148.2, 148.7, 149.5, 158.2, 159.3, 161.8, 164.5, 166.9, 167.0, 194.1. High-resolution MS (ESI): calculated M^+ = 783.1862; observed M^+ = 783.1947.

Synthesis of *fac*-Bis(2-phenylbenzothiazole)-p-hydroxymethyl-2-(pyridyl)-benzene Iridium(III) (8).

Compound **5** (1.00 g, 1.26 mmol) was dissolved in 30 mL of THF, and 3.5 mL (3.5 mmol) of $LiAlH_4$ (1.0 M solution in THF) was added dropwise, upon which the solution gradually turned from bright organge-red to yellow. The reaction mixture was stirred at room temperature for 12 hours and then quenched by the addition of water (200 mL). The resulting solution was extracted twice with CH_2Cl_2 (2 x 100 mL). The organic layers were combined, washed three times with water and dried over magnesium sulfate. The solvent was removed to give the target compound **8**. Yield: 0.95 g (95%). ^1H NMR (300 MHz, $CDCl_3$) (ppm): δ = 4.40 (d, 2H, J = 1.2 Hz), 6.40 (d, 1H, J = 7.8 Hz), 6.56 (d, 1H, J = 1.8 Hz), 6.60 (dd, 1H, J_1 = 7.2 Hz, J_2 = 0.6 Hz), 6.72 (dd, 2H, J_1 = 7.2 Hz, J_2 = 0.6 Hz), 6.80-7.00 (m, 7H), 7.12-7.23 (m, 3H), 7.59-7.80 (m, 6H), 7.86-7.88 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) (ppm): δ = 65.8, 118.8, 119.2, 120.5, 122.5, 126.2, 126.2, 126.7, 131.0, 131.1, 132.6, 132.9, 134.4, 136.5, 136.9, 140.2, 140.8, 142.3, 143.6, 149.1, 151.5, 152.5, 156.8, 159.1, 161.5, 166.4, 179.1, 179.7. High-resolution MS (ESI): calculated M^+ = 797.1146; observed M^+ = 795.1169.

Synthesis of *fac*-Bis(2-phenylquinoline)-p-hydroxymethyl-2-(pyridyl)-benzene Iridium(III) (9).

The same procedure as described above for the preparation of **8** was employed. Yield: 0.97 g (97%). ^1H NMR (300 MHz, $CDCl_3$) (ppm): δ = 4.30 (s, 2H), 6.43 (s, 1H), 6.61 (t, 2H, J = 6.6 Hz), 6.70-6.82 (m, 4H), 6.93-7.16 (m, 3H), 7.19-7.26 (m, 4H), 7.45 (d, 1H, J = 12 Hz), 7.52-7.64 (m, 3H), 7.66-7.76 (m, 4H), 7.84-7.92 (m, 2H), 8.00-8.26 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) (ppm): δ = 65.6, 117.8, 118.0, 118.7, 119.1, 119.8, 120.2, 121.8, 123.5, 125.9, 126.0, 126.7, 126.8, 127.0, 127.3, 127.5, 128.0, 128.7, 129.4, 130.0, 132.1 136.6, 136.7, 137.2, 141.8, 143.0, 144.6, 146.1, 147.9, 148.4, 148.8, 157.2, 158.1, 160.2, 162.9, 165.5, 167.0. High-resolution MS (ESI): calculated M^+ = 785.2018; observed M^+ = 785.2079.

Synthesis of *fac*-Bis(2-phenylpyridine)-4-(pyridin-2-yl)benzyl-hex-5-ynoate Iridium(III) (10).

A mixture of **7** (0.20 g, 0.29 mmol), 5-hexynoic acid (0.15 g, 1.34 mmol), dicyclohexylcarbodiimide (DCC) (0.28 g, 1.34 mmol), and dimethylaminopyridine (DMAP) (0.02 g, 0.16 mmol) in dichloromethane (50 mL) was refluxed for 48 hours under an argon atmosphere. After cooling the reaction to room temperature, the precipitate was filtered off and dissolved with dichloromethane (50 mL). The filtrate was concentrated and precipitated into a large volume of methanol. The residue was collected by filtration and washed with methanol to give the target compound as a yellow solid. Yield: 0.18 g (83%). ^{1}H NMR (300 MHz, $CDCl_3$) (ppm): δ = 1.79 (quintet, 2H, *J* = 7.5 Hz), 1.95 (t, 1H, *J* = 1.8 Hz), 2.23 (dd, 2H, J_1 = 6.9 Hz, J_2 = 2.4 Hz), 2.40 (t, 2H, *J* = 7.5 Hz), 4.91 (s, 2H), 6.74 (s, 1H), 6.80-6.88 (m, 10H), 7.49-7.66 (m, 10H), 7.86 (d, 2H, *J* = 7.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) (ppm): δ = 22.9, 23.6, 32.7, 66.6, 69.0, 83.5, 118.7, 119.1, 121.9, 123.8, 128.8, 129.8, 130.9, 132.4, 135.9, 136.7, 143.6, 147.0, 160.7, 160.9, 161.6, 166.2, 166.6, 172.9. High-resolution MS (ESI): calculated M^+ = 779.2123; observed M^+ = 779.2135.

Synthesis of *fac*-Bis(2-phenylbenzothiazole)-4-(pyridin-2-yl)benzyl-hex-5-ynoate Iridium(III) (11).

The same procedure as described above for the preparation of **10** was employed. Yield: 0.16 g (72%). ^{1}H NMR (300 MHz, CDCl$_3$) (ppm): δ = 1.79 (quintet, 2H, *J* = 6.9 Hz), 1.96 (t, 1H, *J* = 1.8 Hz), 2.22 (dd, 2H, J_1 = 6.9 Hz, J_2 = 2.4 Hz), 2.39 (t, 2H, *J* = 7.5 Hz), 4.89 (s, 2H), 6.39 (d, 1H, *J* = 8.1 Hz), 6.56 (d, 1H, *J* = 1.5Hz), 6.62 (d, 1H, *J* = 7.8 Hz), 6.70 (d, 2H, *J* = 7.8 Hz), 6.72-7.00 (m, 7H), 7.19 (quintet, 3H, *J* = 7.2 Hz), 7.56-7.89 (m, 8H). ^{13}C NMR (75 MHz, CDCl$_3$) (ppm): δ = 23.6, 24.8, 33.0, 66.5, 70.0, 84.7, 118.6, 119.6, 120.1, 121.5, 123.1, 123.5, 123.9, 124.3, 124.6, 125.4, 126.8, 127.5, 132.6, 134.1, 135.6, 136.1, 136.5, 137.0, 140.2, 140.8, 143.9, 150.0, 151.5, 152.5, 156.7, 156.9, 159.0, 161.4, 166.3, 172.9, 179.1, 179.7. High-resolution MS (ESI): calculated M$^+$ = 891.1565; observed M$^+$ = 891.1581.

Synthesis of *fac*-Bis(2-phenyqiunoline)-4-(pyridin-2-yl)benzyl-hex-5-ynoate Iridium(III) (12).

The same procedure as described above for the preparation of **10** was employed. Yield: 0.18 g (80%). ^{1}H NMR (300 MHz, CDCl$_3$) (ppm): δ = 1.83 (quintet, 2H, *J* = 7.5 Hz), 1.99 (t, 1H, *J* = 1.8 Hz), 2.23 (dd, 2H, J_1 = 6.9 Hz, J_2 = 2.4 Hz), 2.39 (t, 2H, *J* = 7.5 Hz), 4.82 (s, 2H), 6.46 (d, 1H, *J* = 1.5 Hz), 6.61-6.81 (m, 7H), 6.87-7.00 (m, 3H), 7.15 (t, 1H, *J* = 6.9 Hz), 7.18 (t, 1H, *J* = 7.1 Hz), 7.37 (d, 1H, *J* = 7.8 Hz), 7.46 (t, 1H, *J* = 7.5 Hz), 7.55 (d, 1H, *J* = 8.7 Hz), 7.57-7.70 (m, 4H), 7.89 (t, 2H, *J* = 8.4Hz), 8.00 (d, 1H, *J* = 8.7 Hz), 8.08 (t, 2H, *J* = 8.1Hz), 8.16 (t, 2H, *J* = 8.7Hz). ^{13}C NMR (75 MHz, CDCl$_3$) (ppm): δ = 18.7, 23.6, 33.0, 66.5, 70.6, 83.6, 117.1, 118.2, 118.6, 118.9, 119.1, 120.8, 121.1, 124.1, 124.6, 125.4, 126.8, 127.5, 128.0, 128.3, 128.7, 129.0, 129.7, 133.5, 136.0, 136.2, 136.5, 137.5, 137.6, 138.1, 138.2, 143.5, 144.6, 146.2, 148.9, 158.1, 160.2, 162.9, 165.5, 167.1, 172.8. High-resolution MS (ESI): calculated M$^+$ = 879.2436; observed M$^+$

= 879.2449. Single-crystal X-ray structure of **12** confirmed that only the facial configuration was obtained.

Synthesis of Poly(styrene)-co-poly(*p*-azidomethyl-styrene) (16).

A solution of **15** (1.00 g, 0.91 mmol based on repeating unit) and NaN_3 (0.50 g, 7.7 mmol) in DMSO (20 mL) were heated at 55 °C for 48 hours. After cooling the reaction mixture to room temperature, it was poured into an excess of water (400 mL). The resulting white precipitate was collected by filtration and washed with water and methanol. Yield: 0.95 g (95%). ^1H NMR (300 MHz, $CDCl_3$) (ppm): δ = 0.94 (broad s), 1.14 (broad s), 1.45 (broad s), 1.87 (broad s), 4.24 (broad s), 6.59 (broad s), 7.09 (broad s). ^{13}C NMR (75 MHz, $CDCl_3$) (ppm): δ = 26.6, 27.9, 31.9, 31.9, 40.3, 42.6, 43.7, 45.9, 46.3, 54.6, 124.7, 125.6, 132.5, 145.2.

Synthesis of Poly(9-vinylcarbazole)-co-poly(*p*-(azidomethyl-styrene) (14).

The same procedure as above for the preparation of **16** was employed. Yield: 0.90 g (90%). ^1H NMR (300 MHz, $CDCl_3$) (ppm): δ = 0.45-1.78 (broad m), 2.60 (broad s), 3.20 (broad s), 3.41 (broad s), 3.86 (broad s), 4.11 (broad s), 4.90 (broad s), 6.38-6.67 (broad m), 6.95 (broad s), 7.71 (broad s). ^{13}C NMR (75 MHz, $CDCl_3$) (ppm): δ = 35.5 38.8, 48.1, 49.9, 54.1, 107.3, 107.9, 110.3, 118.7, 120.1, 121.8, 123.7, 124.9, 127.5, 137.2, 137.6, 139.8.

General Procedure for the Functionalization of all Copolymers via "Click" Chemistry.

A mixture of **14** (0.20 g, 0.10 mmol based on repeating units) or **16** (0.11 g, 0.10 mmol based on repeating unit), 0.10 mmol of **10**, **11**, or **12**, and Cu(I)I (0.005 g, 0.02 mmol) in DMF (20 mL) was stirred for 48 hours at 80 °C. After cooling to room temperature, the reaction mixture was precipitated into a large volume of MeOH (200 mL). The precipitate was collected and washed with MeOH to give the desired fully functionalized copolymers.

Synthesis of 17

Green-yellow solid. Yield: 0.24g (89%). ^{1}H NMR (300 MHz, $CDCl_3$) (ppm): δ = 0.87-2.05 (m, broad), 2.27 (s, broad), 2.65 (s, broad), 3.18 (s, broad), 3.49 (s, broad), 4.92 (s, broad), 6.38 (s, broad), 6.84 (s, broad), 7.50 (s, broad), 7.63(s, broad), 8.03 (s, broad). ^{13}C NMR (75 MHz, $CDCl_3$) (ppm): 11.0, 24.7, 24.9, 25.0, 35.7, 36.3, 36.5, 37.4, 47.7, 49.9, 50.0, 50.2, 66.4, 107.8, 107.9, 108.0, 108.1, 108.2, 110.3, 110.4, 110.5, 118.4, 118.5, 118.6, 118.8, 119.0, 121.9 124.9, 125.0, 125.1, 125.2, 129.8, 130.0, 135.9, 136.0, 136.1, 137.3, 137.4, 137.7, 139.2, 140.0, 143.3, 146.8, 146.9, 147.0, 147.1, 160.6, 161.0, 161.1, 170.0, 173.0.

Synthesis of 18

Yellow solid. Yield: 0.26g (93%). ^{1}H NMR (300 MHz, $CDCl_3$) (ppm): δ = 0.85-1.77 (m, broad), 2.27 (s, broad), 2.64 (s, broad), 3.19 (s, broad), 3.40 (s, broad), 4.87 (s, broad), 6.37 (s, broad), 6.56 (s, broad), 6.85 (s, broad), 7.65 (s, broad), 8.00 (s, broad). ^{13}C NMR (75 MHz, $CDCl_3$) (ppm): δ = 20.0, 24.7, 24.8, 25.0, 33.0, 33.4, 33.5, 35.4, 35.5, 36.4, 38.9, 49.2, 49.8, 49.9, 50.0, 50.2, 50.3, 66.4, 66.5, 107.9, 108.0, 108.1, 110.2, 110.4, 118.5, 118.6, 118.7, 118.8, 118.9, 119.0, 119.1, 120.3, 124.9, 125.0, 125.1, 126.2, 126.7, 131.0, 137.0, 137.1, 137.2, 137.3, 137.4, 137.9, 140.2, 149.1, 149.2, 151.5, 151.6, 152.4, 156.5, 156.7, 156.8, 159.0, 159.0, 161.3, 166.1, 166.2, 172.9, 179.1, 179.6.

Synthesis of 19

Orange solid. Yield: 0.22g (79%). ^{1}H NMR (300 MHz, CDCl$_3$) (ppm): δ = 0.85-1.92 (m, broad), 2.47 (s, broad), 2.60 (s, broad), 3.16 (s, broad), 3.40 (s, broad), 4.77 (s, broad), 6.06 (s, broad), 6.36 (s, broad), 6.57 (s, broad), 6.76 (s, broad), 7.66 (s, broad). ^{13}C NMR (75 MHz, CDCl$_3$) (ppm): δ = 23.2, 24.6, 24.7, 24.9, 25.3, 26.1, 30.8, 32.6, 32.9, 35.3, 36.3, 36.5, 48.0, 49.6, 49.8, 49.9, 50.0, 50.1, 66.0, 107.9, 110.0, 110.2, 118.2, 118.4, 118.5, 118.7, 119.0, 119.2, 119.3, 120.1, 121.7, 121.9, 123.5, 123.6, 123.7, 124.7, 124.9, 125.0, 125.2, 126.0, 127.3, 127.5, 128.4, 129.6, 137.0, 137.2, 137.3, 137.4, 137.5, 127.6, 139.7, 139.8, 139.9, 140.2, 160.9, 166.9, 167.0, 172.4, 174.6.

Synthesis of 20

Green-yellow solid. Yield: 0.16g (85%). ^{1}H NMR (300 MHz, CDCl$_3$) (ppm): δ = 0.95 (s, broad), 1.14 (s, broad), 1.44 (s, broad), 1.86 (s, broad), 2.29 (s, broad), 2.68 (s, broad), 2.90 (s, broad), 2.96 (s, broad), 4.93 (s, broad), 5.29 (s, broad), 5.34 (s, broad), 6.61 (s, broad), 6.86 (s, broad), 7.10 (s, broad), 7.49 (s, broad), 7.62 (s, broad), 7.80(s, broad), 8.05 (s, broad). ^{13}C NMR (75 MHz, CDCl$_3$) (ppm): δ = 24.0, 24.5, 24.8, 25.3, 27.8, 31.4, 33.3, 40.3, 41.5, 42.2, 42.6, 43.6, 44.0, 44.2, 45.7, 53.6, 66.5, 66.7, 103.6, 110.5, 113.1, 117.7, 118.8, 119.8, 121.8, 124.4, 124.6, 125.5, 126.7, 125.5, 128.9, 129.7, 135.8, 135.9, 136.6, 136.9, 143.5, 144.8, 145.0, 145.1, 145.7, 145.9, 146.8, 160.6, 160.9, 165.2, 165.9,166.1, 166.4, 172.4, 172.9.

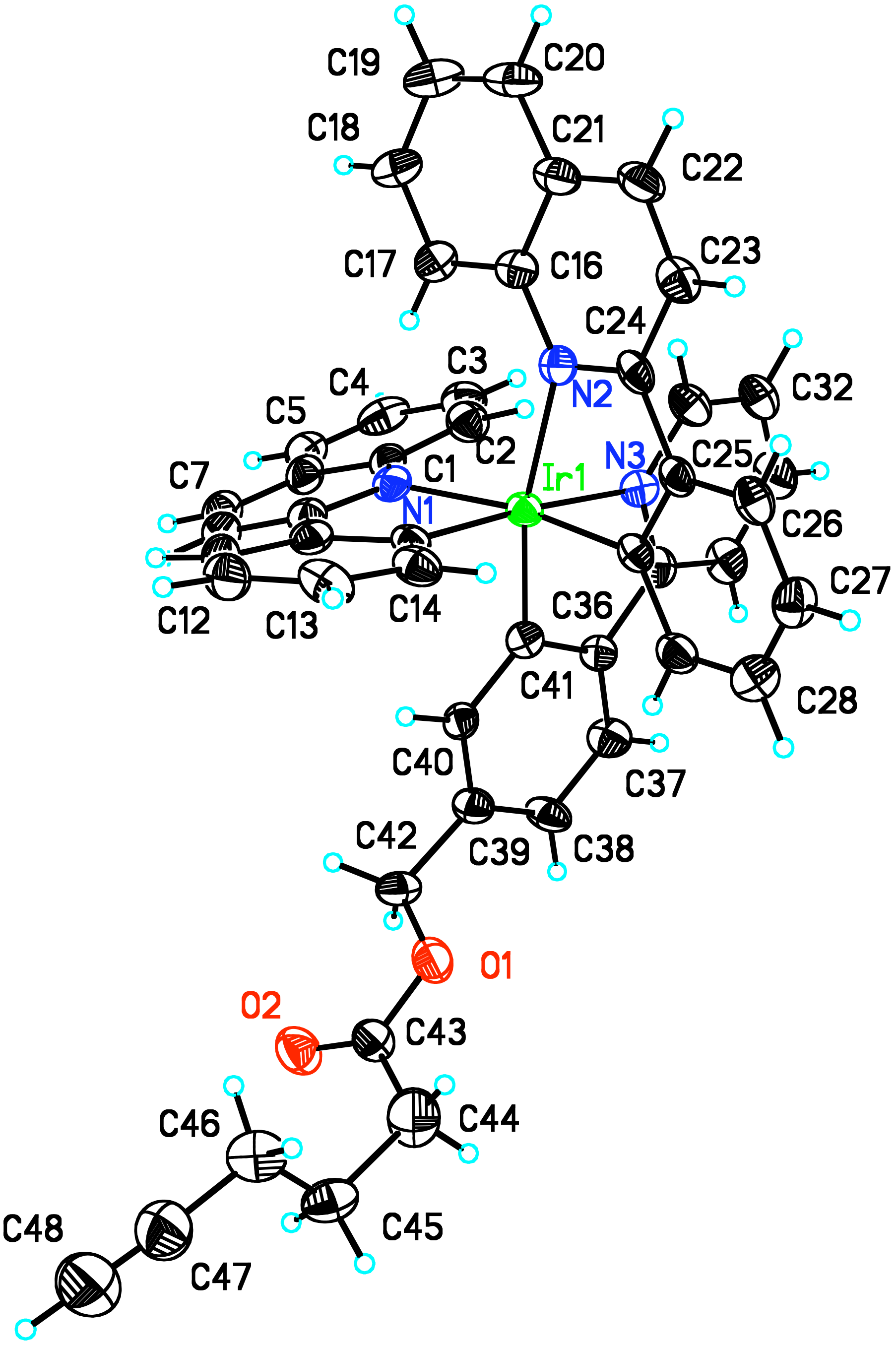
Synthesis of 21

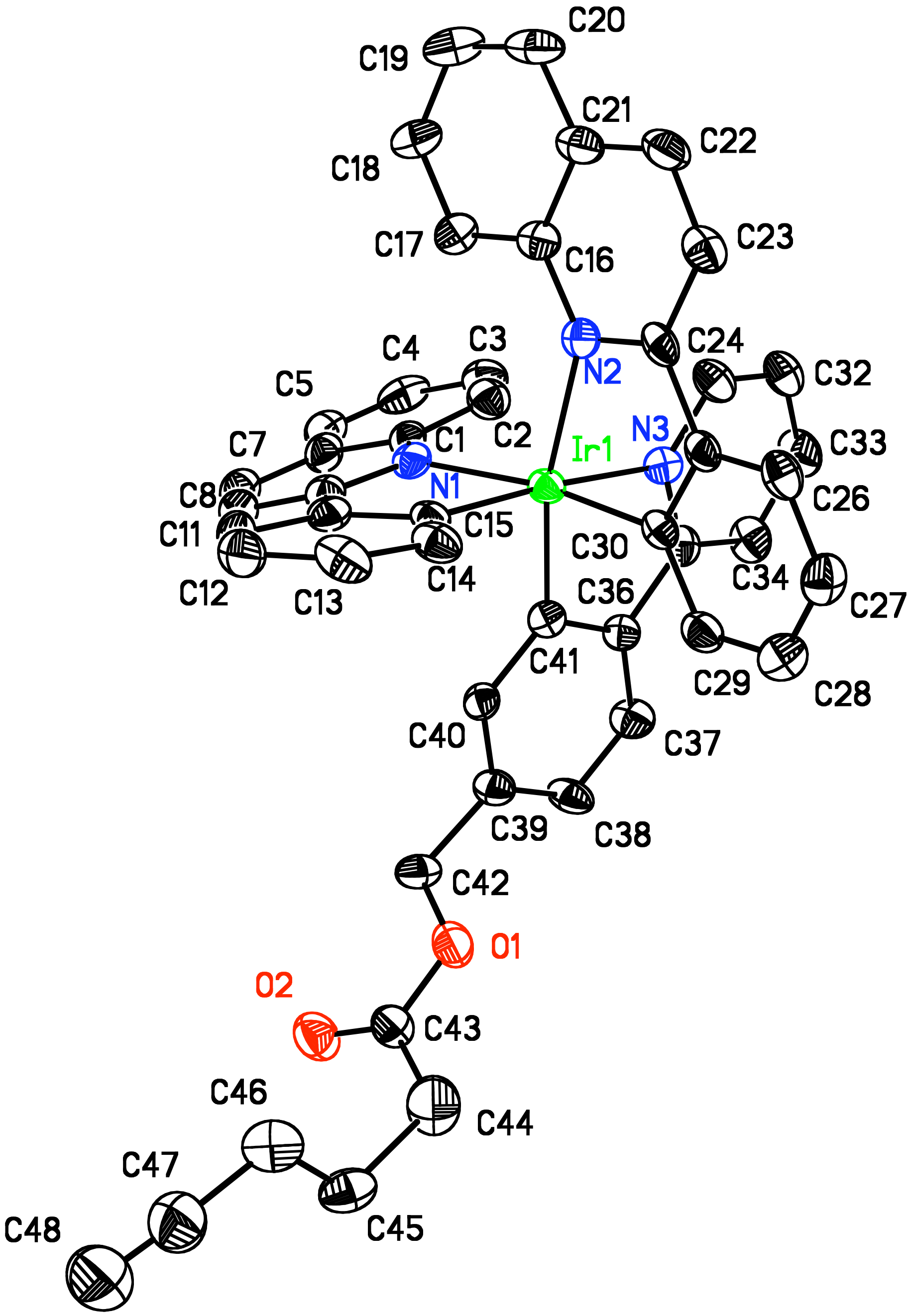
Yellow solid. Yield: 0.17 (86 %). ^{1}H NMR (300 MHz, CDCl$_3$) (ppm): δ = 0.91(s, broad), 1.11 (s, broad), 1.40 (s, broad), 1.81 (s, broad), 2.06 (s, broad), 2.60 (s, broad), 2.90 (s, broad), 2.96 (s, broad), 4.88 (s, broad), 5.27 (s, broad), 6.48 (s, broad), 6.66 (s, broad), 6.81 (s, broad), 7.03 (s, broad), 7.47 (s, broad), 7.49 (s, broad), 7.58 (s, broad), 7.81 (s, broad). ^{13}C NMR (75 MHz, $CDCl_3$) (ppm): δ = 25.5, 27.0, 27.8, 27.9, 29.6, 31.4, 31.8, 40.2, 40.3, 40.7, 43.5, 43.7, 43.8, 44.0, 44.1, 45.7, 66.2, 118.7, 119.4, 122.4, 125.5, 125.6, 126.6, 126.8, 126.9, 127.0, 127.1, 127.3, 127.6, 127.8, 145.0, 145.1, 145.4, 145.7, 151.5, 152.4, 156.6, 158.9, 161.2, 166.2, 172.9, 179.0, 179.6.

Synthesis of 22

Orange solid. Yield: 0.14 (71%). ^{1}H NMR (300 MHz, $CDCl_3$) (ppm): δ = 0.88 (s, broad), 0.93 (s, broad), 1.13 (s, broad), 1.42 (s, broad), 1.78 (s, broad), 2.29 (s, broad), 2.50 (s, broad), 2.70 (s, broad), 3.56 (s, broad), 4.77 (s, broad), 5.26 (s, broad), 6.59 (s, broad), 6.81 (s, broad), 7.07 (s, broad), 7.46 (s, broad), 7.53 (s, broad), 7.64 (s, broad), 7.84 (s, broad), 7.89 (s, broad), 8.10 (s, broad), 8.18 (s, broad), 8.37 (s, broad). ^{13}C NMR (75 MHz, $CDCl_3$) (ppm): δ = 24.6, 24.7, 24.8, 31.4, 39.9, 40.0, 40.2, 40.3, 40.5, 43.5, 43.6, 43.7, 43.9, 45.8, 66.5, 118.1, 119.7, 125.3, 125.5, 125.6, 125.7, 126.8, 127.4, 127.6, 127.9, 144.9, 145.0, 145.1, 145.2, 148.8, 160.2, 162.8, 165.4, 166.9, 167.0, 172.9.

Crystal Structures for Compound 12.

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