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Norbornene-Based Copolymers Containing Platinum Complexes and Bis(carbazolyl)benzene Groups in Their Side-Chains

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ABSTRACT: Two norbornene-functionalized tetradentate cyclometalated platinum(II) complexes were synthesized and copolymerized with a bis(carbazolyl)benzene-based comonomer using ring-opening metathesis polymerization (ROMP). The copolymers are soluble in common solvents and the molecular weights of these copolymers can be well controlled as a result of the living character of the ROMP. The photophysical and electrochemical properties of the copolymers were compared to their corresponding small molecules. The copolymers showed almost identical photophysical and electrochemical properties demonstrating the inertness of the polymer backbone toward the photophysical properties of the tethered platinum complexes. All complexes exhibit bright photoluminescence in the green region with lifetimes around 0.4 μs and solution phosphorescence quantum efficiencies as high as 0.56, which suggest that these materials could be interesting for OLED applications.

Introduction

Numerous cyclometalated platinum(II) complexes[1] possess high phosphorescence efficiencies and hold great promise for applications in optoelectronic devices such as organic light-emitting diodes (OLEDs)[2−6] as a result of their strong spin−orbit coupling. Complexes of metals with 5d electrons (such as Pt) in many cases display rapid intersystem crossing from the lowest excited singlet state to the triplet state, which often has a sufficiently short phosphorescence lifetime that they can luminesce with high efficiency.[7] On the basis of these properties, it is theoretically possible to obtain internal quantum efficiencies of 100% harvesting both triplet and singlet excitons formed by hole and electron recombination in a host material.

Indeed, in recent years platinum complexes have been incorporated into OLED devices. Thompson et al.[1b] described the synthesis and phosphorescent characteristics of a series of phosphorescent cyclometalated platinum(II) complexes of the general structure Pt(C^N)(O^O), (where C^N is a cyclometalated ligand such as 2-phenylpyridine and O^O is a β-diketonate ligand). Inoue, Jabbour, Li and co-workers[1c,1i] reported the characterization of several Pt(N^C^N) structures (where N^C^N reperesents di(2-pyridinyl)benzene-based tridentate ligands) with much higher quantum yield in solution. Recently, Fréchet et al.[1j] reported the first OLED device in which phosphorescent Pt complex moieties are incorporated into a polymer; these polymers were obtained by binding Pt(C^N) building blocks to (O^O) ligands after polymerization.

The fabrication of OLEDs can be carried out using either vapor deposition[8] or solution processing.[9−11] Both processes have advantages and disadvantages. In contrast to the vacuum-deposition route, which is a more costly approach and limited to thermally stable volatile small molecules (which can often be prone to crystallization), the solution-processing approach is potentially a lower cost process that can be applied to materials with high molecular weight and low volatility, such as dendrimers and polymers, but may be accompanied by poorer performance associated with impurities from the solvent or from the increased difficulties of purifying materials of this type. Solution-processing can be problematic when mixtures of materials are required for a particular layer of a device; for example, phase separation in blends of small-molecule phosphors with polymers can lead to aggregation and subsequent luminescence quenching and device degradation. To reduce the impacts of aggregation, a promising methodology is based on the covalent anchoring of phophors (such as Ir or Pt complexes) to the same polymer backbone as the host material, resulting in single-component materials that can be solution-processed.

We have been interested in side-chain-functionalized polymers, especially poly(norbornene)s, as key materials for optoelectronic devices such as OLEDS, since these materials allow for fine-tuning of the polymeric structures as a result of the often living character of the ring-opening metathesis polymerization (ROMP).[12,13] Furthermore, many materials based on poly(norbornene) can be readily solution-processed.[14] Finally, the functional group tolerance of most ruthenium olefin metathesis initiators is excellent, allowing for the direct covalent grafting of metal complexes onto poly(norbornene)s. We have reported poly(norbornene)s covalent modified with both iridium(III) and platinum(II) complexes.[12a−12d] However, we found that for the Pt(C^N)(O^O) system, the ruthenium initiators decompose partially during the polymerization, most likely due to transfer of the acetylacetonate ligand from platinum to ruthenium.[12a] To further extend this research, we designed a robust tetradentate polypyridyl ligand to construct doubly cyclometalated platinum complexes with potential applications in solution-processed OLEDs.[1k] In this contribution, we describe the synthesis of random copolymers containing 3,5-di(carbazol-9-yl)benzene-type host moieties and platinum complexes in the side-chains that emit green light with high efficiency and report their solution

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and solid-state photoluminescence properties. The photophysical and electrochemical properties observed in copolymers were almost identical to those of their corresponding small molecular platinum complexes. The good phosphorescence quantum efficiency suggests that this material could be of interest for OLED applications.

Experimental Section

General Data. All experiments with air- and moisture-sensitive intermediates and compounds were carried out under an inert atmosphere using standard Schlenk techniques. NMR spectra were recorded on either a 400 MHz Varian Mercury spectrometer or a 400 MHz Bruker AMX 400 and referenced using the residual proton signal of the solvent. UV−vis absorption spectra were recorded on a Varian Cary 5E UV−vis−NIR spectrophotometer, while solution and thin-film PL spectra were recorded on a Fluorolog III ISA spectrofluorometer. Lifetime measurements were taken using a PTI model C-72 fluorescence laser spectrophotometer with a PTI GL-3300 nitrogen laser. Cyclic voltammograms were obtained on a computer controlled BAS 100B electrochemical analyzer, and measurements were carried out under a nitrogen flow in deoxygenated DMF solutions of tetra-*n*-butylammonium hexafluorophosphate (0.1 M). Glassy carbon was used as the working electrode, a Pt wire as the counter electrode, and an Ag wire anodized with AgCl as the pseudoreference electrode. Potentials were referenced to the ferrocenium/ferrocene ($FeCp_2^{+/0}$) couple by using ferrocene as an internal standard. 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 eluent on American Polymer Standards 10 μm particle size, linear mixed bed packing columns. The flow rate used for all measurements was 1 mL/min, and the GPCs were calibrated using poly(styrene) standards. Differential scanning calorimetry (DSC) data were collected using a Seiko model DSC 220C. Thermal gravimetric analysis (TGA) data were collected using a Seiko model TG/DTA 320.

Bis(2-(6-bromopyridyl)ketone (**1**),[15] 1,1-bis(6-bromo-2-pyridyl)ethan-1-ol (**2**),[16] 1,1-bis(6-bromo-2-pyridyl)-1-fluoroethane (**6**),[16] 5-(5-bromopentyl)bicyclo[2.2.1]hept-2-ene (mixture of *endo* and *exo* isomers, **9**),[17] $PtCl_2(PhCN)_2$,[18] 3,5-diiodobenzoic acid (**18**),[19] and methyl 3,5-diiodobenzoate (**19**)[19] were synthesized according to published procedures. Other reagents and solvents were used as received without further purification. Inductively coupled plasma-mass spectrometry (ICP−MS) for platinum and ruthenium was provided by Bodycote Testing Group.

1,1-Bis(6-bromo-2-pyridyl)-1-methoxyethane (3). 1,1-Bis-(6-bromo-2-pyridyl)ethan-1-ol (1.00 g, 2.79 mmol) was added to a suspension of sodium hydride (0.50 g, 20.8 mmol) in 40 mL of THF. When the evolution of hydrogen gas had ceased, iodomethane (1.30 mL, 20.8 mmol) was added. After the mixture was stirred for 2 h, the reaction was quenched with 10% aqueous HCl until acidic and then basified with 10% aqueous potassium carbonate. The crude product was extracted with dichloromethane (50 mL × 3) and dried over anhydrous magnesium sulfate. Finally, a silica gel column purification (hexane:EtOAc = 5:1) gave a white solid (0.75 g, 2.02 mmol, yield 72%). TLC, R_f = 0.55 (hexane:EtOAc = 5:1). MS (EI): m/z = 372 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 (d, 2H, J = 1.6 Hz), 7.47 (s, 2H), 7.29 (dd, 2H, J = 5.2 and 2.9 Hz), 3.21 (s, 3H), 1.97 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 164.36, 140.83, 138.62, 126.52, 120.17, 82.69, 51.12, 21.72.

1,1-Bis(6-(2,4-difluorophenyl)-2-pyridyl)-1-methoxyethane (4). Compound **3** (0.71 g, 1.91 mmol), 2,4-difluorophenylboronic acid (1.20 g, 7.60 mmol) and tetrakis(triphenylphosphine)-palladium(0) (0.25 g, 0.216 mmol) were added to a round-bottomed flask equipped with a reflux condenser and dissolved in 20 mL of THF. After 15 mL of aqueous 2 N Na_2CO_3 was delivered, the reaction mixture was refluxed for 24 h. The cooled crude mixture was poured onto water and extracted with CH_2Cl_2 (50 mL × 3) and then dried over anhydrous magnesium sulfate. Finally, a silica gel column purification (hexane:EtOAc = 10:1) gave a transparent oil (0.73 g, 1.67 mmol, yield 88%). TLC, R_f = 0.65 (hexane:EtOAc = 8:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03 (dt, 2H, J = 10 and 6.8 Hz), 7.70 (d, 2H, J = 7.6 Hz), 7.65 (ddd, 2H, J = 8.0 and 2.0 and 1.2 Hz), 7.54 (dd, 2H, J = 8.0 and 1.0 Hz), 6.84−6.96 (m, 4H), 3.34 (s, 3H), 2.17 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 163.53, 161.94 (dd, J = 224 and 12 Hz), 159.43 (dd, J = 225 and 12 Hz), 150.51 (d, J = 3 Hz), 136.76, 132.29 (dd, J = 10 and 5 Hz), 123.62 (dd, J = 11 and 4 Hz), 122.02 (d, J = 11 Hz), 119.84, 111.54 (dd, J = 21 and 4 Hz), 103.87 (dd, J = 27 and 25 Hz), 84.08, 51.28, 22.01. ^{19}F NMR (376 MHz, $CDCl_3$) δ: −110.55 (F position 2 with respect to phenylpyridine), −113.07 (F position 4 with respect to phenylpyridine).

[1,1-Bis(6-(4,6-difluorophenyl)-2-pyridyl-*N*,C^2)-1-methoxyethane]-platinum(II) (5). A mixture of compound **4** (200 mg, 0.46 mmol), $PtCl_2(PhCN)_2$ (220 mg, 0.46 mmol) and xylene (15 mL) was refluxed for 60 min under an argon flow. The xylene was removed by distillation and the crude product was purifed by silica gel column chromatography (dichloromethane) to give compound **5** as a yellow solid (145 mg, 0.23 mmol, yield 50%). TLC, R_f = 0.6 (hexane: dichloromethane = 1:1). FAB-MS: m/z = 631.1 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.10 (d, 2H, J = 8.4 Hz), 7.95 (pseudo t, 2H, J = 8.0 Hz), 7.73 (dd, 2H, J = 8.0 and 1.0 and 1.2 Hz), 7.54 (dd, 2H, J = 10 and 2.4 Hz), 6.56−6.64 (m, 4H), 3.47 (s, 3H), 1.95 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 162.89 (d, J = 7 Hz), 161.99 (dd, J = 252 and 12 Hz), 160.01, 159.42 (dd, J = 255 and 12 Hz), 152.76 (d, J = 5 Hz), 139.28, 130.23 (pseudo t, J = 3 Hz), 121.38 (d, J = 21 Hz), 119.50, 117.39 (dd, J = 18 and 3 Hz), 99.87 (pseudo t, J = 27 Hz), 89.05, 53.57, 33.76. ^{19}F NMR (376 MHz, $CDCl_3$) δ: −108.35 (F position 2 with respect to phenylpyridine), −110.95 (F position 4 with respect to phenylpyridine). ^{195}Pt NMR (86 MHz, $CDCl_3$) δ: −3583 (referenced to aqueous K_2PtCl_4). Anal. Calcd for $C_{25}H_{16}F_4N_2OPt$: C, 47.55; H, 2.55; N, 4.44. Found: C, 47.50; H, 2.55; N, 4.41.

1,1-Bis(6-(2,4-difluorophenyl)-2-pyridyl)-1-fluoroethane (7). Compound **6** (0.68 g, 1.89 mmol), 2,4-difluorophenylboronic acid (1.20 g, 7.60 mmol) and tetrakis(triphenylphosphine)-palladium(0) (0.25 g, 0.216 mmol) were added to a round-bottomed flask equipped with a reflux condenser and dissolved in 20 mL of THF. After the addition of 15 mL of aqueous 2 N Na_2CO_3, the reaction mixture was refluxed for 24 h. The cooled crude mixture was poured onto water and extracted with CH_2Cl_2 (50 mL × 3) and then dried over anhydrous magnesium sulfate. Finally, a silica gel column purification (hexane:EtOAc = 10:1) gave a transparent oil (0.71 g, 1.66 mmol, yield 88%). TLC, R_f = 0.75 (hexane:EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11 (dt, 2H, J = 10 and 6.8 Hz), 7.76 (m, 4H), 7.56 (d, 2H, J = 7.2 Hz), 6.86−7.00 (m, 4H), 2.33 (d, 3H, J = 12 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 162.05 (dd, J = 235 and 12 Hz), 161.14 (d, J = 27 Hz), 159.54 (dd, J = 236 and 12 Hz), 151.05, 137.10, 132.31 (dd, J = 10 and 5 Hz), 123.34 (dd, J = 11 and 4 Hz), 122.76 (d, J = 11 Hz), 118.65 (d, J = 7 Hz), 111.59 (dd, J = 21 and 4 Hz), 103.95 (dd, J = 27 and 25 Hz), 97.95 (d, J = 172 Hz), 25.28 (d, J = 3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ: −109.95 (F position 2 with respect to phenylpyridine), −112.91 (F position 4 with respect to phenylpyridine), −146.66.

[1,1-Bis(6-(4,6-difluorophenyl)-2-pyridyl-*N*,C^2)-1-fluoroethane]-platinum(II) (8). A mixture of compound **7** (200 mg, 0.47 mmol), $PtCl_2(PhCN)_2$ (225 mg, 0.48 mmol), and xylene (15 mL) was refluxed for 60 min under an argon flow. The xylene was removed by distillation and the crude product was purified by silica gel column chromatography (dichloromethane) to give compound **8** as a yellow solid (170 mg, 0.27 mmol, yield 59%). TLC, R_f = 0.65 (hexane:dichloromethane = 1:1). MALDI−TOF MS: m/z = 619.1 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11 (d, 2H, J = 8.4 Hz), 7.96 (pseudo t, 2H, J = 8.2 Hz), 7.66 (d, 2H, J = 8.0 Hz),

7.54 (d, 2H, J = 10 Hz), 6.62 (pseudo t, 4H, J = 9.8 Hz), 2.12 (d, 3H, J = 24 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 162.84 (d, J = 5 Hz), 162.38 (dd, J = 228 and 12 Hz), 159.81 (dd, J = 229 and 12 Hz), 158.03 (d, J = 30 Hz), 152.06 (d, J = 6 Hz), 139.49, 130.07 (pseudo t, J = 3 Hz), 121.89 (d, J = 21 Hz), 117.28 (dd, J = 18 and 2 Hz), 116.83 (d, J = 15 Hz), 100.06 (pseudo t, J = 26 Hz), 99.86 (d, J = 181 Hz), 33.56 (d, J = 13 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ: −107.64 (F position 2 with respect to phenylpyridine), −110.47 (F position 4 with respect to phenylpyridine), 167.22. ^{195}Pt NMR (86 MHz, $CDCl_3$) δ: −3613 (referenced to aqueous K_2PtCl_4). Anal. Calcd for $C_{24}H_{13}F_5N_2Pt$: C, 46.53; H, 2.12; N, 4.52. Found: C, 46.34; H, 2.05; N, 4.53.

Bis(6-bromo-2-pyridyl)(5-(bicyclo[2.2.1]hept-5-en-2-yl)pentyl)-methanol (Mixture of *endo* and *exo* Isomers) (10). Compound **9** (1.30 g, 5.35 mmol) and magnesium (0.26 g, 10.7 mmol) was stirred for 4 h in 40 mL of THF under an argon flow. The obtained Grignard reagent (norbornenylmagnesium bromide) was added to a THF (20 mL) solution of compound **1** (0.90 g, 2.63 mmol) via a cannula. After the mixture was stirred for 2 h, the reaction was quenched with 1 mL of methanol followed by 5 mL of 10% aqueous ammonium chloride. The crude product was extracted with dichloromethane (30 mL × 3 times) and dried over anhydrous magnesium sulfate. Finally, a silica gel column purification (hexane:EtOAc = 7:1) gave a yellow oil (0.85 g, 1.68 mmol, yield 64%). TLC, R_f = 0.75 (hexane:EtOAc = 5:1). The *endo* isomer: ^1H NMR (400 MHz, $CDCl_3$) δ: 7.82 (d, 2H, J = 7.6 Hz), 7.53 (pseudo t, 2H, J = 8.0 Hz), 7.32 (d, 2H, J = 7.6 Hz), 6.06 (dd, 1H, J = 5.6 and 3.2 Hz), 5.86 (dd, 1H, J = 5.6 and 3.2 Hz), 5.78 (s, 1H), 2.70 (m, 2H), 2.25 (m, 2H), 1.90 (m, 1H), 1.78 (m, 1H), 0.90−1.42 (m, 10H), 0.38−0.47 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 164.53, 139.98, 139.14, 136.74, 132.38, 126.35, 119.92, 77.92, 49.46, 45.29, 42.42, 42.02, 38.60, 34.60, 32.32, 29.89, 28.41, 23.41.

Bis(6-bromo-2-pyridyl)(5-(bicyclo[2.2.1]hept-5-en-2-yl)pentyl)-methoxymethane (Mixture of *endo* and *exo* Isomers) (11). Compound **10** (0.85 g, 1.68 mmol) was added to a suspension of sodium hydride (0.30 g, 12.5 mmol) in 40 mL of THF. Iodomethane (0.80 mL, 12.8 mmol) was added as the evolution of hydrogen gas had ceased. The mixture was stirred for 2 h, the reaction was quenched with 10% aqueous HCl until it became acidic, and then basified with 10% aqueous potassium carbonate. The crude product was extracted with dichloromethane (30 mL × 3) and dried over anhydrous magnesium sulfate. Finally, a silica gel column purification (hexane:EtOAc = 7:1) gave a yellow oil (0.63 g, 1.21 mmol, yield 72%). TLC, R_f = 0.6 (hexane:EtOAc = 5:1). MS (EI): m/z = 520 (M^+). The *endo* isomer: ^1H NMR (400 MHz, $CDCl_3$) δ: 7.42−7.50 (m, 4H), 7.25 (dd, 2H, J = 6.8 and 2.0 Hz), 6.04 (dd, 1H, J = 6.0 and 3.0 Hz), 5.85 (dd, 1H, J = 6.0 and 3.0 Hz), 3.11 (s, 3H), 2.70 (m, 2H), 2.55 (m, 2H), 1.90 (m, 1H), 1.77 (m, 1H), 0.90−1.42 (m, 10H), 0.39−0.46 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 163.94, 140.80, 138.35, 136.63, 132.28, 126.28, 120.72, 84.60, 50.52, 49.39, 45.21, 42.33, 38.53, 34.52, 32.26, 31.83, 29.80, 28.45, 22.41.

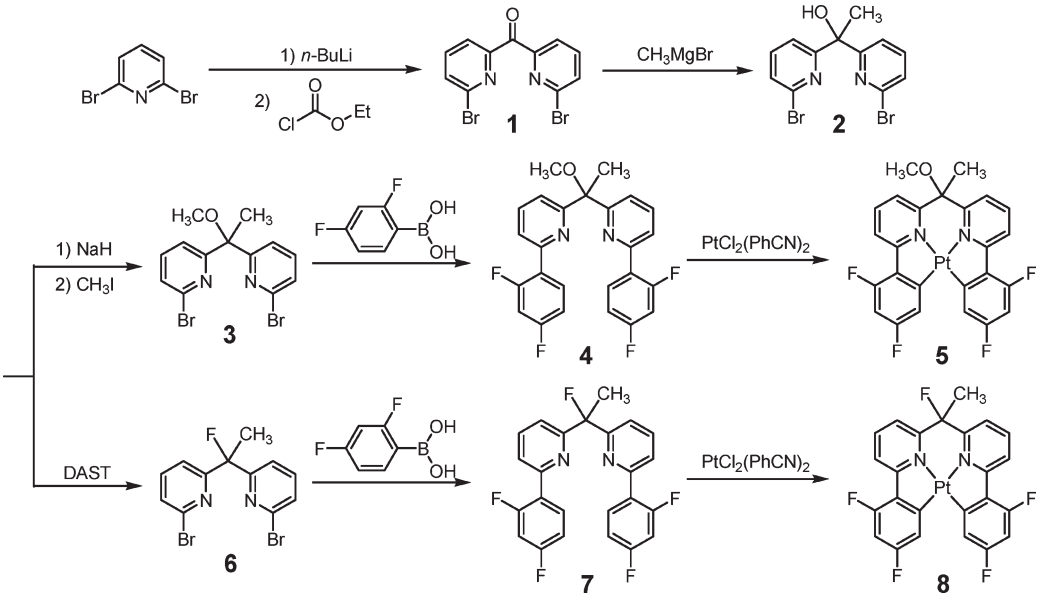
Bis(6-(2,4-difluorophenyl)-2-pyridyl)(5-(bicyclo[2.2.1]hept-5-en-2-yl)pentyl)methoxymethane (Mixture of *endo* and *exo* Isomers) (12). Compound **11** (0.63 g, 1.21 mmol), 2,4-difluorophenylboronic acid (0.75 g, 4.75 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.16 g, 0.138 mmol) were added to a round-bottomed flask equipped with a reflux condenser and dissolved in 20 mL of THF. After the addition of 15 mL of aqueous 2 N Na_2CO_3, the reaction mixture was refluxed for 24 h. The cooled crude mixture was poured onto water, extracted with CH_2Cl_2 (50 mL × 3) and dried over anhydrous magnesium sulfate. Finally, a silica gel column purification (hexane:EtOAc = 10:1) gave a transparent oil (0.63 g, 1.07 mmol, yield 88%). TLC, R_f = 0.7 (hexane:EtOAc = 8:1). The *endo* isomer: ^1H NMR (400 MHz, $CDCl_3$) δ: 8.02 (dt, 2H, J = 10 and 6.8 Hz), 7.68 (d, 2H, J = 8.0 Hz), 7.63 (d, 2H, J = 8.0 Hz), 7.53 (d, 2H, J = 8.0 Hz), 6.82−6.97 (m, 4H), 6.06 (dd, 1H, J = 5.6 and 3.2 Hz), 5.86 (dd, 1H, J = 5.6 and 2.8 Hz), 3.26 (s, 3H), 2.78 (m, 2H), 2.70 (m, 2H), 1.89 (m, 1H), 1.77 (m, 1H), 0.90−1.44 (m, 10H), 0.40−0.46 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 163.06, 161.92 (dd, J = 222 and 12 Hz), 159.41 (dd, J = 223 and 12 Hz), 150.45 (d, J = 3 Hz), 136.72, 136.52, 132.34, 132.27 (dd, J = 9 and 5 Hz), 123.66 (dd, J = 11 and 3 Hz), 121.77 (d, J = 11 Hz), 120.37, 111.50 (dd, J = 21 and 4 Hz), 104.10 (dd, J = 24 and 24 Hz), 85.99, 50.68, 49.46, 45.30, 42.44, 38.65, 34.69, 32.32 (2C), 30.23, 28.64, 22.80. ^{19}F NMR (376 MHz, $CDCl_3$) δ: −109.97 (F position 2 with respect to phenylpyridine), −112.38 (F position 4 with respect to phenylpyridine).

[Bis(6-(4,6-difluorophenyl)-2-pyridyl-*N*,*C*^{2})(5-(bicyclo[2.2.1]-hept-5-en-2-yl)pentyl)methoxymethane]platinum(II) (Mixture of *endo* and *exo* Isomers) (13). A mixture of compound **12** (200 mg, 0.34 mmol), $PtCl_2(PhCN)_2$ (165 mg, 0.34 mmol) and xylene (15 mL) was refluxed for 60 min under an argon flow. The xylene was removed by distillation and the crude product was purified by silica gel column chromatography (dichloromethane) to give compound **13** as a yellow solid (100 mg, 0.13 mmol, yield 38%). TLC, R_f = 0.7 (hexane:dichloromethane = 1:1). MALDI−TOF MS: m/z = 779.2 (M^+). The *endo* isomer: ^1H NMR (400 MHz, $CDCl_3$) δ: 8.15 (d, 2H, J = 8.0 Hz), 7.98 (pseudo t, 2H, J = 8.0 Hz), 7.73 (dd, 2H, J = 8.0 and 0.8 Hz), 7.57 (dd, 2H, J = 10 and 2.0 Hz), 6.62 (ddd, 2H, J = 12, 8.8, and 2.0 Hz), 6.01 (dd, 1H, J = 5.6 and 3.2 Hz), 5.76 (dd, 1H, J = 5.8 and 3.0 Hz), 3.41 (s, 3H), 2.58 (d, 2H, J = 28 Hz), 2.23 (m, 4H), 0.70−1.94 (m, 10H), 0.29−0.34 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 162.92 (d, J = 7 Hz), 162.07 (dd, J = 254 and 12 Hz), 159.42 (dd, J = 255 and 12 Hz), 158.65, 153.20 (d, J = 5 Hz), 138.85, 136.80, 132.23, 130.23 (pseudo t, J = 3 Hz), 121.36 (d, J = 21 Hz), 120.87, 117.54 (dd, J = 18 and 2 Hz), 99.83 (pseudo t, J = 27 Hz), 92.79, 53.81, 49.46, 47.26, 45.27, 42.44, 38.50, 34.45, 32.31, 29.28, 28.07, 23.29. ^{19}F NMR (376 MHz, $CDCl_3$) δ: −108.13 (F position 2 with respect to phenylpyridine), −110.80 (F position 4 with respect to phenylpyridine). ^{195}Pt NMR (86 MHz, $CDCl_3$) δ: −3602 (referenced to aqueous K_2PtCl_4). Anal. Calcd for $C_{36}H_{32}F_4N_2OPt$: C, 55.45; H, 4.41; N, 3.59. Found: C, 55.74; H, 4.19; N, 3.45.

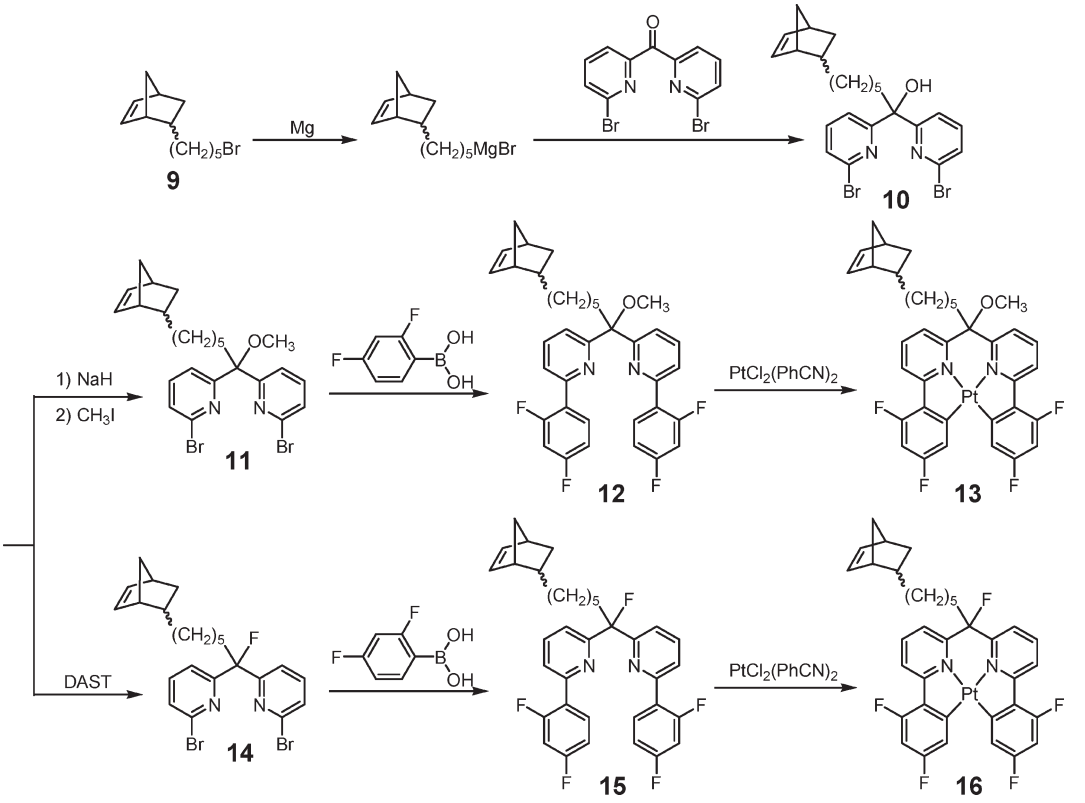
Bis(6-bromo-2-pyridyl)(5-(bicyclo[2.2.1]hept-5-en-2-yl)pentyl)-fluoromethane (Mixture of *endo* and *exo* Isomers) (14). Diethylaminosulfur trifluoride (DAST, 0.46 mL, 3.72 mmol) was added to a dichloromethane (20 mL) solution of compound **10** (0.65 g, 1.28 mmol) at 0 °C. After the mixture was stirred at room temperature for 60 min, it was quenched with 10 mL of ice-cooled water (caution: strongly exothermic reaction) and then basified with 10 mL 3 M sodium hydroxide. The crude product was extracted with dichloromethane (30 mL × 3) and dried over anhydrous magnesium sulfate. Finally, a silica gel column purification (hexane:EtOAc = 10:1) gave a yellow oil (0.58 g, 1.14 mmol, yield 88%). TLC, R_f = 0.65 (hexane:EtOAc = 5:1). The *endo* isomer: ^1H NMR (400 MHz, $CDCl_3$) δ: 7.52 (m, 4H), 7.36 (dd, 2H, J = 7.0 and 1.8 Hz), 6.06 (dd, 1H, J = 5.6 and 3.2 Hz), 5.86 (dd, 1H, J = 5.8 and 3.0 Hz), 2.70 (m, 2H), 2.51 (m, 2H), 1.91 (m, 1H), 1.78 (m, 1H), 0.90−1.40 (m, 10H), 0.40−0.47 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 161.05 (d, J = 26 Hz), 141.22 (d, J = 2 Hz), 138.81, 136.74, 132.33, 127.20, 119.37 (d, J = 8 Hz), 97.87 (d, J = 179 Hz), 49.44, 45.27, 42.40, 38.56, 37.78 (d, J = 21 Hz), 34.50, 32.31, 29.65, 28.30, 22.85 (d, J = 3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ: −161.34.

Bis(6-(2,4-difluorophenyl)-2-pyridyl)(5-(bicyclo[2.2.1]hept-5-en-2-yl)pentyl)fluoromethane (Mixture of *endo* and *exo* Isomers) (15). Compound **14** (0.60 g, 1.18 mmol), 2,4-difluorophenylboronic acid (0.80 g, 4.75 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.14 g, 0.121 mmol) were added to a round-bottomed flask equipped with a reflux condenser and dissolved in 20 mL of THF. After the addition of 15 mL of aqueous 2 N Na_2CO_3, the reaction mixture was refluxed for 24 h. The cooled crude mixture was poured onto water, extracted with CH_2Cl_2 (50 mL × 3 times) and dried over anhydrous magnesium sulfate. Finally, a silica gel column purification (hexane:EtOAc = 10:1) gave a transparent oil (0.60 g, 1.04 mmol, yield 88%). TLC,

Scheme 1. Syntheses of Platinum Complexes 5 and 8



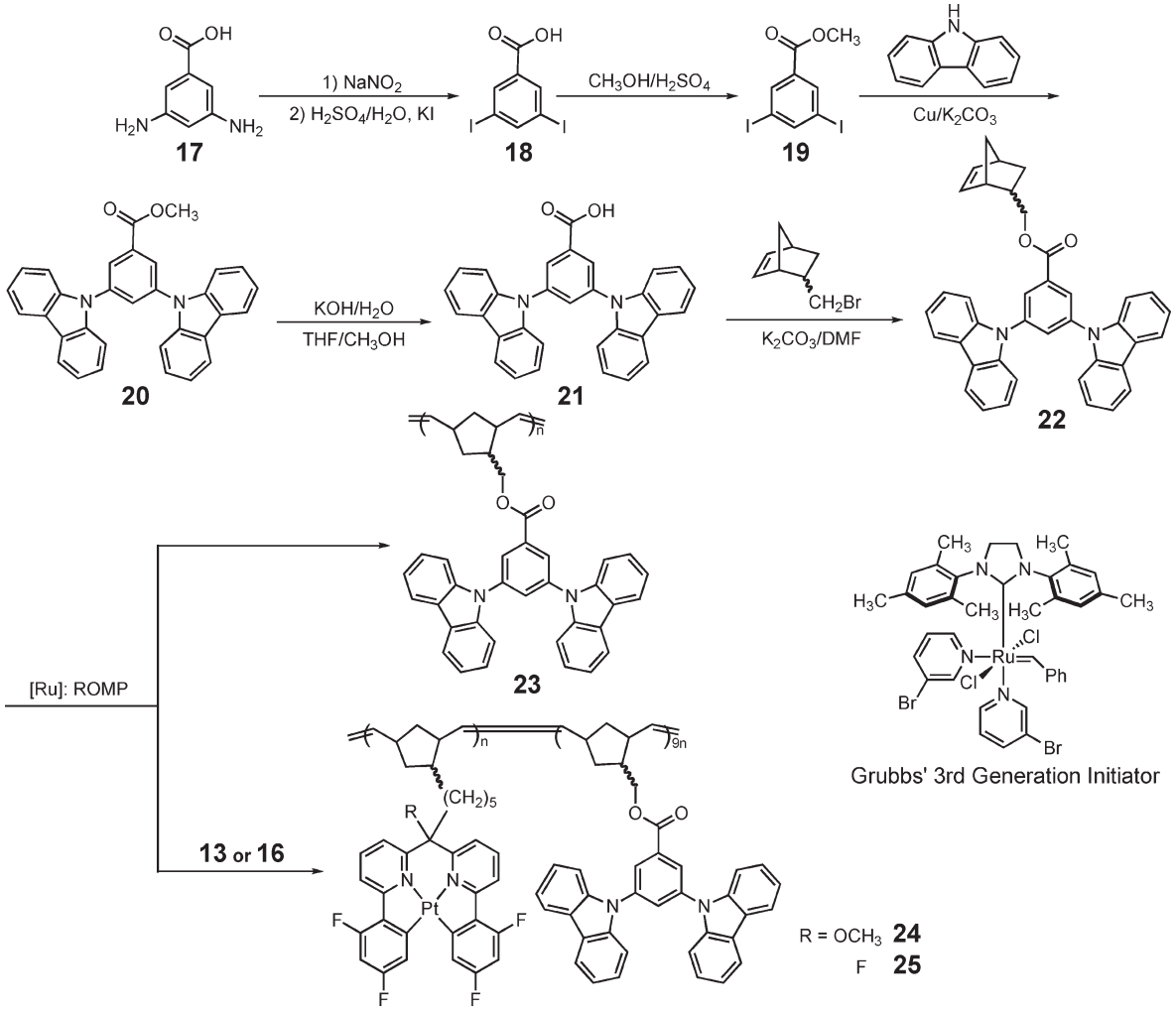
Scheme 2. Syntheses of Platinum Complexes Containing Monomers 13 and 16



R_f = 0.8 (hexane:EtOAc = 5:1). The *endo* isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.13 (dt, 2H, J = 10 and 6.8 Hz), 7.74 (m, 4H), 7.56 (d, 2H, J = 7.2 Hz), 6.85−7.00 (m, 4H), 6.08 (dd, 1H, J = 5.6 and 3.0 Hz), 5.87 (dd, 1H, J = 6.0 and 2.8 Hz), 2.78 (m, 2H), 2.71 (m, 2H), 1.92 (m, 1H), 1.79 (m, 1H), 0.95−1.47 (m, 10H), 0.42−0.48 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 162.07 (dd, J = 230 and 12 Hz), 160.61 (d, J = 27 Hz), 159.56 (dd, J = 232 and 12 Hz), 151.03, 136.99, 136.79, 132.40 (dd, J = 10 and 5 Hz), 132.35, 123.43 (dd, J = 11 and 4 Hz), 122.50 (d, J = 11 Hz), 118.85 (d, J = 8 Hz), 111.57 (dd, J = 21 and 4 Hz), 103.97 (dd, J = 27 and 25 Hz), 99.85 (d, J = 176 Hz), 49.51, 45.37, 42.50, 38.69, 38.02 (d, J = 21 Hz), 34.64, 32.93, 30.01, 28.47, 23.24 (d, J = 3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ: −110.04 (F position 2 with respect to phenylpyridine), −112.85 (F position 4 with respect to phenylpyridine), −162.31 (bridge position).

[Bis(6-(4,6-difluorophenyl)-2-pyridyl-*N*,*C*^{2})(5-(bicyclo[2.2.1]-hept-5-en-2-yl)pentyl)fluoromethane]platinum(II) (Mixture of *endo* and *exo* Isomers) (16). A mixture of compound **12** (200 mg, 0.35 mmol), $PtCl_2(PhCN)_2$ (165 mg, 0.35 mmol) and xylene (15 mL) was refluxed for 60 min under an argon flow. The xylene was removed by distillation and the crude product was purified by silica gel column chromatography (dichloromethane) to give **16** as a yellow solid (80 mg, 0.10 mmol, yield 30%). TLC, R_f = 0.7 (hexane:dichloromethane = 1:1). FAB-MS: m/z = 768.2

Scheme 3. Syntheses of Carbazole Monomer 22 and Polymers 23−25



$(M+1)^+$. The *endo* isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.10 (d, 2H, J = 8.4 Hz), 7.94 (pseudo t, 2H, J = 8.0 Hz), 7.63 (dd, 2H, J = 7.8 and 1.8 Hz), 7.55 (dd, 2H, J = 10 and 2.0 Hz), 6.61 (ddd, 2H, J = 12, 8.8, and 2.0 Hz), 6.02 (dd, 1H, J = 5.6 and 3.0 Hz), 5.78 (dd, 1H, J = 5.8 and 3.0 Hz), 2.60 (d, 2H, J = 26 Hz), 2.50 (m, 4H), 0.73−1.93 (m, 10H), 0.31−0.37 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 162.83 (d, J = 6 Hz), 162.38 (dd, J = 226 and 12 Hz), 159.81 (dd, J = 229 and 12 Hz), 157.24 (d, J = 30 Hz), 152.07 (d, J = 7 Hz), 139.07, 136.85, 132.24, 130.10 (pseudo t, J = 3 Hz), 121.76 (d, J = 21 Hz), 117.81 (d, J = 16 Hz), 117.25 (dd, J = 18 and 2 Hz), 101.97 (d, J = 181 Hz), 100.03 (pseudo t, J = 27 Hz), 49.48, 45.29, 45.16 (d, J = 23 Hz), 42.45, 38.53, 34.42, 32.33, 29.03, 28.17, 22.87 (d, J = 2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ: −107.54 (F position 2 with respect to phenylpyridine), −110.45 (F position 4 with respect to phenylpyridine), 157.15 (bridge position). ^{195}Pt NMR (86 MHz, $CDCl_3$) δ: −3610 (referenced to aqueous K_2PtCl_4). Anal. Calcd for $C_{35}H_{29}F_5N_2Pt$: C, 54.76; H, 3.81; N, 3.65. Found: C, 54.46; H, 3.79; N, 3.53.

Methyl 3,5-di(carbazol-9-yl)benzoate (20). To a stirred solution of methyl 3,5-diiodobenzoate (3.00 g, 7.73 mmol), carbazole (3.00 g, 17.94 mmol), Cu (6.40 g, 100.7 mmol), and 18-crown-6 (65 mg, 0.25 mmol) in 30 mL 1,2-dichlorobenzene was added potassium carbonate (12.60 g, 91.17 mmol) under a nitrogen flow. The reaction was stirred at 180 °C for 10 h then cooled to room temperature, filtered and the solid residues were washed with THF. After the solvents were removed by evaporation from the combined filtration solution, the crude product was purified by silica gel column chromatography using toluene as the eluent. The target compound was obtained as a white product in 72% yield (2.60 g, 5.58 mmol) by recrystallization from acetone/methanol. MS (EI): m/z = 466 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.37 (d, 2H, J = 1.6 Hz), 8.15 (dd, 4H, J = 7.2 and 0.8 Hz), 8.02 (t, 1H, J = 1.6 Hz), 7.52 (dd, 4H, J = 7.2 and 0.8 Hz), 7.45 (td, 4H, J = 7.2 and 1.6 Hz), 7.32 (td, 4H, J = 7.2 and 1.2 Hz), 3.99 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 165.39, 140.18, 139.54, 133.63, 129.09, 126.45, 126.20, 123.62, 120.55, 120.43, 109.42, 52.82. Anal. Calcd for $C_{32}H_{22}N_2O_2$: C, 82.38; H, 4.75; N, 6.00. Found: C, 82.34; H, 4.66; N, 6.03.

3,5-Di(carbazol-9-yl)benzoic acid (21). A mixture of methyl 3,5-di(carbazol-9-yl)benzoate (1.00 g, 2.14 mmol), 2 mL of aqueous KOH (30 wt %), 15 mL of THF, and 10 mL of methanol was stirred at room temperature for 5 h. After the organic solvent was removed under reduced pressure, 20 mL of methanol and 80 mL of 2 M aqueous HCl were added subsequently to the residues. The reaction mixture was stirred for an additional hour. A pale yellow solid was obtained by filtration. The crude product was purified by recrystallization from acetone/water in 98% yield (0.95 g, 2.10 mmol). MS (EI): m/z = 452.1 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.37 (d, 2H, J = 2.4 Hz), 8.21 (dt, 4H, J = 7.2 and 0.8 Hz), 8.19 (t, 1H, J = 2.4 Hz), 7.63 (dd, 4H, J = 7.2 and 0.8 Hz), 7.47 (td, 4H, J = 7.2 and 1.2 Hz), 7.30 (td, 4H, J = 7.2 and 1.2 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 166.04, 141.19, 140.34, 135.14, 130.08, 127.31, 127.11, 124.38, 121.32, 121.17, 110.42.

Bicyclo[2,2,1]hept-5-en-2-ylmethyl 3,5-di(carbazol-9-yl)benzoate (Mixture of *endo* and *exo* Isomers) (22). A mixture of 3,5-di(carbazol-9-yl)benzoic acid (0.50 g, 1.10 mmol), 5-(bromomethyl)bicyclo[2,2,1]hept-2-ene (0.30 g, 1.60 mmol), potassium carbonate

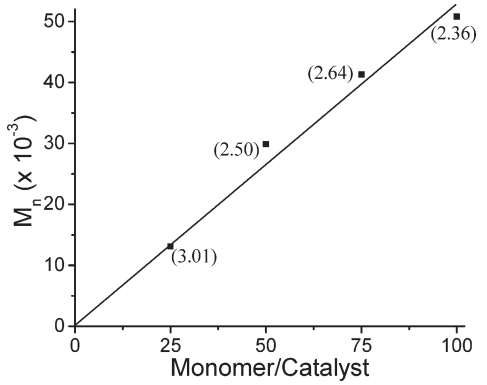


Figure 1. Plot of M_n vs monomer to catalyst ratio for the ROMP of **22**. Numbers in parentheses are the polydispersity indices of the polymers.

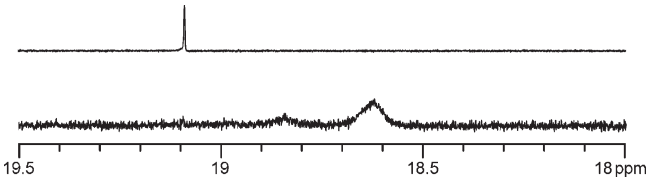


Figure 2. Carbene ^{1}H NMR signals for the third-generation Grubbs initiator (top), and during the polymerizations of **22** (bottom).

Table 1. Polymer Characterization Data of 23−25

polymer	M_n	M_w	PDI	T_g (°C)	T_d (°C)[a]	Pt (%)[b,c]	Ru (ppm)[b]
23	30 000	75 000	2.50	189	387		
24	27 000	72 000	2.64	189	382	2.05 (2.50)	9.7
25	27 000	74 000	2.74	187	380	1.77 (2.54)	8.6

[a] Temperature at 5% weight loss. [b] ICP−MS measurements. [c] The values in parentheses are the feed ratios.

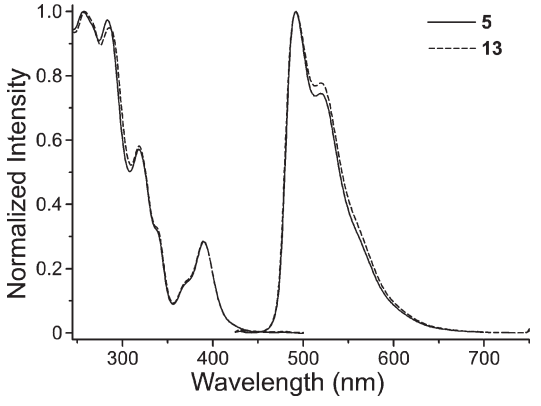


Figure 3. Comparison of the absorption and photoluminescence spectra between **5** and **13** in CH_2Cl_2.

(4.00 g, 28.94 mmol) and 6 mL of DMF was stirred at 60 °C for 26 h. After the reaction mixture was cooled to room temperature, 40 mL of water was added. A white solid was obtained by filtration which was purified by silica gel column chromatography using toluene and hexanes (3:2) as eluents. The isolated glassy solid was dissolved in a small mount of acetone (2 mL) and added dropwise to a mixture of methanol and water (20 mL, 4:1) to give a white precipitate. After filtration and drying, host monomer **22** (0.48 g, 0.86 mmol, yield 78%) was obtained. MS (EI): m/z = 558.2 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.38 (m, 2H), 8.16 (d, 4H, J = 7.2 Hz), 8.19 (m, 1H), 7.53 (d, 4H, J = 7.2 Hz), 7.46 (t, 4H, J = 7.2 Hz), 7.33 (t, 4H, J=7.2 Hz), 6.19 (dd, 0.7H, J=5.6 and 2.4 Hz, *endo*), 6.09 (m, 0.6H, *exo*), 6.00 (dd, 0.7H, J = 5.6 and 1.4 Hz,

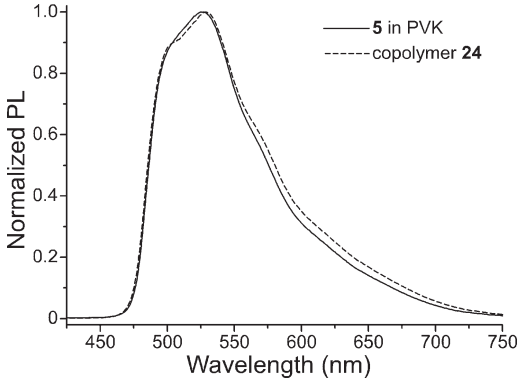


Figure 4. Comparison of the solid-state photoluminescence spectra between **5** in PVK and copolymer **24**.

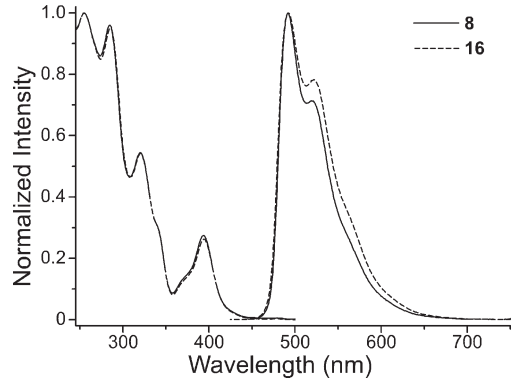


Figure 5. Comparison of the absorption and photoluminescence spectra between **8** and **16** in CH_2Cl_2.

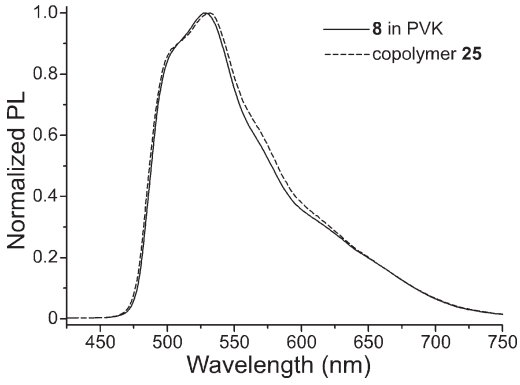


Figure 6. Comparison of the solid-state photoluminescence spectra of **8** in PVK and copolymer **25**.

endo), 4.49 (dd, 0.3H, J = 10.4 and 6.8 Hz, *exo*), 4.33 (dd, 0.3H, J = 9.2 and 9.2 Hz, *exo*), 4.18 (dd, 0.7H, J = 10.4 and 6.8 Hz, *endo*), 4.00 (dd, 0.7H, J = 10.8 and 9.2 Hz, *endo*), 2.87 (m, 2H), 2.53 (m, 1H), 1.88 (m, 1H), 1.45 (m, 2H), 0.67 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 165.01, 140.31, 139.62, 137.82 (*endo*), 136.98 (*exo*), 136.12 (*exo*), 134.16, 132.06 (*endo*), 129.09, 126.51, 126.31, 123.69, 120.63, 120.53, 109.48, 69.80 (*exo*), 69.16 (*endo*), 49.40 (*endo*), 44.97 (*exo*), 43.93 (*endo*), 43.65 (*exo*), 42.17 (*endo*), 41.57 (*exo*), 37.98 (*exo*), 37.77 (*endo*), 29.55 (*exo*), 28.92 (*endo*). Anal. Calcd for $C_{39}H_{30}N_2O_2$: C, 83.85; H, 5.41; N, 5.01. Found: C, 83.89; H, 5.35; N, 4.98.

General Polymerization Procedure. A solution of Grubbs' third-generation initiator[14e] in CH_2Cl_2 (~ 0.01 M) was added to a methylene chloride solution (~0.02 M) containing a mixture of **22** and the desired platinum-containing monomer (**13** or **16**) in a ratio of 9:1 (wt %), respectively. The reaction mixture was

Table 2. Photophysical Characterization of 5, 8, 13, 16, 24, and 25

entry	λ_{abs}/nm ($\varepsilon/10^3$ L·mol^{-1}·cm^{-1})[a]	λ_{em} (nm)[a]	λ_{em} (nm)	Φ_f[c]	Φ_f[d]	τ/μs[c]
5	257 (33.2), 284 (32.3), 319 (19.0), 339 (10.5), 368 (4.92), 390 (9.42), 478 (0.89)	493, 525, 560 (sh)	526[b]	0.54	0.55	0.38
13	258 (33.3), 285 (31.6), 318 (19.3), 339 (10.8), 369 (5.24), 390 (9.52), 477 (0.81)	492, 520, 560 (sh)		0.56	0.54	0.39
24			528			
8	255 (33.8), 284 (32.4), 320 (18.4), 340 (10.3), 369 (4.41), 394 (9.27), 478 (0.78)	492, 520, 564 (sh)	526[b]	0.58	0.57	0.32
16	255 (33.6), 285 (33.4), 321 (18.2), 341 (10.0), 370 (4.25), 394 (8.84), 478 (0.77)	492, 522, 564 (sh)		0.55	0.56	0.38
25			529			

[a] In CH_2Cl_2. [b] In PVK films. [c] In degassed CH_2Cl_2; reference: *fac*-Ir(ppy)$_3$ (Φ = 0.40 in toluene). [d] In degassed THF; reference: *fac*-Ir(ppy)$_3$ (Φ = 0.40 in toluene).

stirred for 20 min at ambient temperature. After complete monomer conversion, the polymerization was quenched by the addition of ethyl vinyl ether and stirred for an additional 20 min. The reaction mixture was concentrated and precipitated into methanol. The resulting solid was collected by filtration, redissolved in methylene chloride, and reprecipitated into methanol. This procedure was repeated five times until the hexane solution was clear to yield polymers **23**, **24**, and **25** for which ^{1}H NMR spectra showed no remaining monomer or other impurity signals. The polymers were synthesized with a total monomer to catalyst ratio of 50:1.

Polymer 23. ^{1}H NMR ($CDCl_3$) δ: 8.24 (br, 2H), 8.01 (br, 4H), 7.89 (br, 1H), 7.42 (br, 4H), 7.31 (br, 4H), 7.20 (br, 4H), 5.11 (br, 2H), 4.06 (br, 2H), 2.17−1.01 (m, 7H). Anal. Calcd for $(C_{39}H_{30}N_2O_2)_n$: C, 83.85; H, 5.41; N, 5.01. Found: C, 83.62; H, 5.35; N, 4.94.

Polymer 24. ^{1}H NMR ($CDCl_3$) δ: 8.24 (br, 2.2H), 8.02 (br, 4.2H), 7.89 (br, 1.2H), 7.42 (br, 4.2H), 7.32 (br, 4H), 7.20 (br, 4H), 6.52 (br, 0.2H), 5.09 (br, 2.2H), 4.06 (br, 2H), 3.16 (br, 0.3H), 2.60−0.87 (m, 8.7H). ICP−MS: Pt, 2.05% (detection limit 0.5 ppm); Ru, 9.7 ppm (detection limit 0.2 ppm).

Polymer 25. ^{1}H NMR ($CDCl_3$) δ: 8.22 (br, 2.2H), 8.01 (br, 4.2H), 7.87 (br, 1.2H), 7.41 (br, 4.2H), 7.31 (br, 4H), 7.19 (br, 4H), 6.51 (br, 0.2H), 5.09 (br, 2.2H), 4.07 (br, 2H), 2.63−0.89 (m, 8.7H). ICP−MS: Pt, 1.77% (detection limit 0.5 ppm); Ru, 8.6 ppm (detection limit 0.2 ppm).

Quantum-Mechanical Calculations. The molecular geometries were optimized using spin-restricted Density Functional Theory (DFT) calculations for the ground state (S_0) and spin-unrestricted DFT calculations for the lowest triplet excited state (T_1), based on the B3LYP hybrid exchange-correlation functional. The LANL2DZ effective core potential and basis set are employed for the platinum atom while for the ligands we considered the 6-31G* basis set in the course of geometry optimizations and the more extended 6-31+G* basis set for energy calculations. All optimized geometries were confirmed to correspond to absolute minima by evaluating the vibrational frequencies. Adiabatic triplet energies were obtained based on the optimized structures of the S_0 and T_1 states via the Δ*S*CF method. The absorption energies to higher singlet states were also computed using time-dependent DFT (TD-DFT). Natural transition orbital (NTO) analyses[20] were also performed to clarify the nature of the singlet absorptions. All calculations were performed with the TURBOMOLE package.[21]

Results and Discussion

Synthesis. The platinum complexes **5** and **8** as well as the functionalized norbornenes **13** and **16** were synthesized as described in Schemes 1 and 2. The reaction between bis(2-(6-bromopyridyl))ketone (**1**) and a Grignard reagent (norbornenylpentyl magnesium bromide) is the key step for the synthesis of the platinum complex-based monomers since this step affords the norbornene-functionalized intermediates with an alcohol at the bridge position. The alcohol group can then be treated with either sodium hydride followed by iodomethane to install a methoxy group or with DAST (diethylaminosulfur trifluoride) to fluorinate the compound that improves the thermal stability of the final products. The ligands tethered to norbornenes (**12** and **15**) were obtained via Suzuki coupling between the dibromo-intermediates (**11** and **14**) and 2,4-difluorophenylboronic acid. Metalation with $PtCl_2(PhCN)_2$ yielded the target platinum complex-based monomers **13** and **16**. The synthesis of platinum complexes **5** and **8** was carried out analogously.

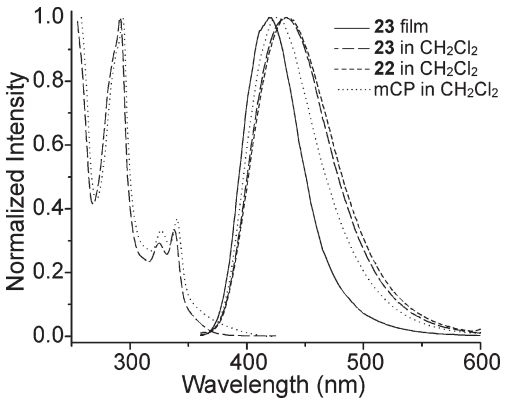


Figure 7. Absorption and photoluminescence spectra of **22**, **23**, and mCP.

As a host monomer for copolymerization with **13** and **16**, we synthesized a norbornene derivative of so-called mCP (1,3-di(carbazol-9-yl)benzene), which has previously been used as a host for fabricating blue-emitting OLEDs due to its high triplet energy (3.0 eV).[1] To avoid complications arising from thermal instability of norbornenyl methyl esters under high-temperature Ullmann-type conditions required for the formation of the aryl-N bonds, we first reacted methyl 3,5-diiodobenzoate (**19**) with carbazole at 180 °C to obtain methyl 3,5-di(carbazol-9-yl)benzoate (**20**), and then hydrolyzed the acid group to get 3,5-di(carbazol-9-yl)benzoic acid (**21**). Compound **21** was esterified with norbornenylmethyl bromide to yield monomer **22** (Scheme 3).

We investigated the ring-opening metathesis polymerization (ROMP), as well as the living character of the polymerization, of the host monomer (**22**) using Grubbs' third-generation initiator. Four different polymerizations were carried out with monomer to initiator ratios of 25:1, 50:1, 75:1, and 100:1. Figure 1 shows the molecular weights of these homopolymers versus the monomer to initiator ratios. A linear relationship was obtained indicating that the polymerization is controlled. Furthermore, ^{1}H NMR spectroscopy experiments showed complete disappearance of the carbene signal of the initiator around 19.10 ppm, and the formation of two new, broad carbene signals at 18.61 (*endo* isomer) and 18.84 (*exo* isomer) ppm, indicating complete initiation (Figure 2). Both experiments suggest that the ROMP of **22** proceeds in a living fashion.

Attempts to investigate the living character of the ROMP of **13** and **16** were not possible because the addition of the ruthenium initiator to the monomer solutions resulted in insoluble materials. We have previously proposed that aggregation may occur in homopolymers and oligomers of

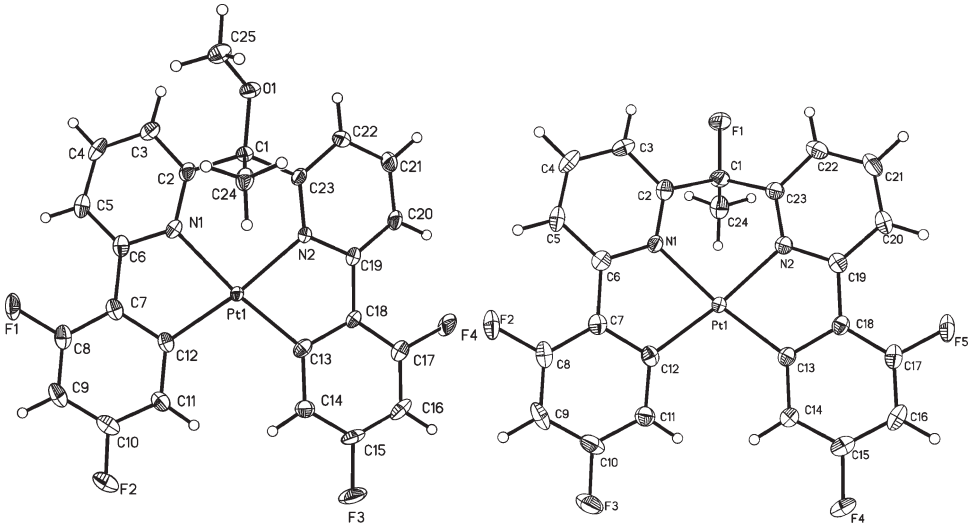


Figure 8. ORTEP views (50% probability) of complexes **5** and **8**.

platinum complex-based polymers, due to the close proximity of the platinum complexes to each other along the polymer backbone.[12a] Therefore, in addition to serving as a host for the phosphors in all the copolymers, **22** also plays a key role as a solubilizing spacer unit between the metal complexes.

Copolymerizations of **13** or **16** with **22** were carried out in distilled methylene chloride at room temperature for 20 min using Grubbs' third-generation initiator (Scheme 3). The ratio of **22** to the platinum complex-containing monomers was 9:1 (wt %). Monomer to initiator ratios of 50:1 were employed. In our previous study, attempts of block copolymerizations of platinum- or iridium-containing monomers and a solubilizing monomer resulted in insoluble mterials[12] indicating that a random distribution of the monomers is necessary to obtain soluble materials. Copolymers **24** and **25** are highly soluble in common organic solvents suggesting a random distribution of the two monomers. All copolymers were characterized by gel-permeation chromatography (Table 1). Molecular weights around 27 kDa and polydispersity indices around 2.7 were obtained. The platinum content feed ratios of copolymers **24** and **25** are 2.50% and 2.54% respectively, slightly larger than the experimental data of 2.05% and 1.77% measured using ICP−MS. We have observed this phenomenon previously when polymerizing phosphorescent metal complexes.[12] We also investigated whether the materials contain any ruthenium residues left from the initiators. Ruthenium contents in all copolymers are below 10 ppm, suggesting good removal of the initiator from the copolymers. Compared to our previous work on Pt(C^N)(O^O) compounds[12a] the doubly cyclometalated Pt moieties are quite stable upon ROMP. All polymers showed glass-transition temperatures around 190 °C and good thermal stabilities with decomposition temperatures above 380 °C at 5% weight loss.

Photophysical Properties. Norbornene-substituted platinum complex **13** exhibits intense vibronic-structured absorption bands at wavelengths below 350 nm with extinction coefficients (ε) on the order of 10^4 $L \cdot mol^{-1} \cdot cm^{-1}$ and a medium intensity band in the region around 390 nm. These two bands can be ascribed to the intra ligand transition and the transition from the metal-centered d orbitals to π^* orbitals of the ligand, respectively. The absorption properties were found to follow Beer's law below concentrations of 5×10^{-4} M suggesting the absence of significant complex aggregation. Compound **13** emits between 460 and 620 nm with λ_{max} at 492 nm, consistent with a triplet metal-to-ligand charge-transfer (^{3}MLCT) excited state. The related lifetime is 0.39 μs and the solution phosphorescence quantum efficiency is 0.56 in THF. This value is slightly higher than that reported for the widely used green emitter $Ir(ppy)_3$ in toluene ($\Phi = 0.40$),[7] suggesting that this material might have interesting properties for OLED applications.

The comparison of the absorption and photoluminescence spectra between **5** and **13** in CH_2Cl_2 is shown as Figure 3. Platinum complex **5** exhibits an almost identical spectrum to monomer **13**. This trend holds true in thin solid films of these compounds. The comparison of the solid-state photoluminescence spectra between copolymer **24** and complex **5** in poly(*N*-vinylcarbazole) (PVK) is shown as Figure 4. Again, the polymeric materials exhibit emission that follows that of their small molecule analogues very well. Similar results were obtained for the other system based on **8**, **16**, and **25**, shown in Figures 5 and 6. All the photophysical characterization data are listed in Table 2. Calculations based on an NTO analysis for compounds **5** and **8** were also performed to clarify the nature of singlet absorptions (Table S1 in Supporting Information) and provide good agreement with experiment. Figures S4 and S5 (Supporting Information) give the NTO description of the nature of the electronic transitions from the singlet ground state to the lowest singlet excited states in compounds **5** and **8**. NTO pictures associated with the triplet emission of respective compounds are also depicted in Figure S6. The corresponding hole-to-electron wave function analyses confirm the characterization of these transitions as MLCT.

We also compared the absorption and photoluminescence spectra of **22**, **23**, and mCP (Figure 7), both of the absorption and photoluminescence spectra are very similar. It suggests that the excited states of monomer **22** and polymer **23** have similar energy-transfer abilities as their mCP analogues. The norbornene-functionalized mCP and corresponding polymer appear to be suitable candidates as hosts for the platinum complexes.

Electrochemistry and Crystallography. The electrochemical properties of the norbornene-substituted platinum complexes **13** and **16** were studied using cyclic voltammetry and the obtained data were compared to those for the corresponding platinum complexes **5** and **8**. All complexes show an irreversible reduction process at peak potentials in the range −1.96 to

Table 3. Redox potentials of 5, 8, 13 and 16

entry[a]	E_{red} (V)	E_{ox} (V)	$E_{ox} - E_{red}$ (V)
5	−2.15	+0.81	2.96
13	−2.11	+0.82	2.93
8	−2.00	+0.87	2.87
16	−1.96	+0.90	2.86

[a] CV in 0.1 M $^{n}Bu_4NPF_6$ DMF solution; scan rate: 50 mV/s; internal reference: $Cp_2Fe^{+/0}$; all the E_{red} and E_{ox} are irreversible.

−2.15 V (vs $Cp_2Fe^{+/0}$), are presumably attributable to molecular reduction localized on the cyclometalated tetradentate ligand. The complexes also show an irreversible, presumably metal-based, oxidation peak with an E_{ox} between +0.81 and +0.90 V, (the oxidation of square-planar complexes is typically irreversible because of rapid solvolysis of the resultant platinum(III) species[22]). Comparison of the potentials in Table 3 indicates that the electrochemical properties of the complexes are not significantly affected by the choice of a fluoro or methoxy group on the bridging position of the ligand or by incorporation of an alkylnorbornene moiety onto the ligand backbone. This is not particularly surprising since both fluoro and methoxy are inductively electron-withdrawing and there is no possibility for π-electron donation through the sp^3 bridging atom. The host monomer **22** has irreversible electrochemistry (E_{ox} = + 0.60 V vs $Cp_2Fe^{+/0}$ in CH_2Cl_2 at scanning rate of 50 mV/s) similar to that of mCP.

Single crystals of complexes **5** and **8** were obtained (Figure 8) from the diffusion of hexane into methylene chloride solutions, and the crystallographic data are shown in Tables S2 and S3 (Supporting Information). The selected geometric parameters indicate that for both complexes the coordination environment of the platinum centers are slightly distorted square planar: the Pt−C bonds (∼2.00 Å) are shorter than the Pt−N bonds (∼2.07 Å) and the bond lengths are in the range of normally observed values for analogous compounds. The structures are π-stacked with distances of ca. 3.4 Å between the planes of adjacent molecules, the interplanar spacing is typically seen in the solid state for some of these square-planar platinum complexes.

Conclusion

In this contribution, we have reported the design and synthesis of two norbornene-functionalized tetradentate cyclometalated platinum(II) monomers and a bis(carbazolyl)-benzene-type host-monomer. Corresponding copolymers can be obtained with molecular weights in the tens of thousands, PDIs around 2.5 and good thermal stabilities via living ROMP as characterized by NMR spectroscopy, GPC and DSC/TGA. The photophysical and electrochemical properties of all copolymers were characterized and compared to their small molecule analogues. In all cases, almost identical photophysical and electrochemical properties were obtained suggesting that the norbornene repeating unit does not alter the properties of the tethered platinum complexes. All complexes exhibit bright photoluminescence in green-light region with lifetime around 0.4 μs and solution phosphorescence quantum efficiency as high as 0.56, which suggests that these materials might be interesting for OLED applications. Further work to incorporate these green-lighting polymers into OLED devices is in progress.

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Supporting Information Available: Figures showing ^{1}H NMR spectra of polymers **23**−**25** and NTO analysis and tables of theoretical singlet absorption energies and oscillator strengths and crystallographic data for **5** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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