

# Synthesis and Characterization of Polymerizable Phosphorescent Platinum(II) Complexes for Solution-Processible Organic Light-Emitting Diodes

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A norbornene-functionalized derivative of acetylacetonate has been used to synthesize a series of new polymerizable norbornene-derivatized phosphorescent platinum complexes of the form Pt(C $\wedge$ N)(O $\wedge$ O\*) where C $\wedge$ N represents a cyclometalated ligand and O $\wedge$ O\* represents the functionalized acetylacetonate ligand. The complexes have been fully characterized, and the structures of three examples have been determined by X-ray diffraction. Solution absorption and luminescence spectra and electrochemical data are very similar to those for analogues without these polymerizable groups. A 9,9-dialkyl-2,7-di(carbazol-9-yl)fluorene material, in which one of the alkyl groups bears a norbornene group, has been synthesized and copolymerized with the Pt(C $\wedge$ N)(O $\wedge$ O\*) complexes using Grubbs ruthenium catalysts, resulting in copolymers with broad molecular weight distributions. The copolymers have been used as lumophores in organic light-emitting diodes, thus demonstrating that platinum phosphors can be successfully integrated into the “hybrid” approach to organic light-emitting diodes, in which molecules with transport or luminescent properties are covalently attached to electronically inert polymer backbones to give solution-processible materials. Emission from aggregate states appears to play a similar role in these copolymers to that seen in vapor-deposited devices based on small phosphor and host molecules; in particular, considerable aggregate emission is observed when a phosphor with blue solution emission is used in the devices.

## Introduction

Organic light-emitting diodes (OLEDs) are a promising technology for thin-film displays due to recent rapid progress in material design and device fabrication.<sup>1</sup> Recombination of a hole and an electron can give rise to either singlet or triplet excited states of the lumophore. In typical organic materials, the triplet is nonluminescent and so only the charge-recombination events that form singlets can result in luminescence. However, due to strong spin–orbit coupling, complexes of the 5d metals display rapid intersystem crossing from the lowest excited singlet state to the lowest triplet state, which often has a sufficiently short phosphorescence lifetime that it can luminesce with high efficiency; thus, formation of either singlet or triplet excited states of the complex results in luminescence. Hence, complexes of this type have been incorporated into OLEDs to harvest both singlet and triplet charge recombinations; theoretically, the internal quantum efficiency of such phosphorescent devices can approach 100%.<sup>2</sup> High phosphorescence

efficiencies have been obtained in OLEDs incorporating complexes of iridium(III),<sup>3</sup> platinum(II),<sup>4</sup> osmium(II),<sup>5</sup> rhenium(I),<sup>6</sup> and ruthenium(II).<sup>7</sup>

Organic light-emitting diodes (OLEDs) fall into two main classes: those based on vacuum-deposited small molecules and those based on solution-processible conjugated polymers. Phosphorescent lumophores have been incorporated into both vacuum-deposited small-molecule devices<sup>8</sup> and conjugated polymer systems.<sup>9</sup> However, there are some problems associated

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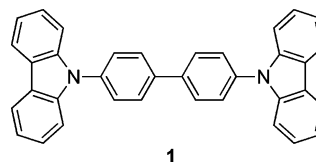
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with phase separation in blends of small-molecule phosphors and polymers; this can lead to aggregation and subsequent luminescence quenching and device degradation. To reduce these effects, iridium phosphors have been covalently attached to the side chains of a fully conjugated polyfluorene backbone,<sup>10</sup> and bis-cyclometalated iridium acetylacetonate units have been incorporated into the conjugated main chains of oligomeric 9,9-dialkylfluorenes.<sup>11</sup>

A third approach to OLEDs utilizes solution-processible side-chain polymers or dendrimers in which the side chains are functionalized with small molecules that have transport or luminescent properties;<sup>12,13</sup> here the ease of solution processing is retained, while the electronic properties of materials can be tuned through the choice of small molecule from among the wide range of well-studied examples and the rheological properties of the polymer may be tuned through the choice of polymer backbone and through copolymerization with other monomers. Tokito et al.<sup>14</sup> have reported random copolymers in which phosphorescent iridium complexes and carbazole units are attached as pendant groups to a polyethylene backbone. Dendritic frameworks have been utilized to lead to solution-processible phosphorescent light-emitting films.<sup>15</sup> The synthesis of norbornene monomers with covalently attached phosphorescent iridium complexes has recently been reported, along with homopolymers and copolymers with norbornenes functionalized with long alkyl chains.<sup>16</sup>

Chart 1. Structure of CBP, 1



1

Brooks et al.<sup>17</sup> reported the synthesis and characterization of a series of phosphorescent cyclometalated organometallic platinum complexes of the general structure  $Pt(C\wedge N)(O\wedge O)$ , where  $C\wedge N$  is a cyclometalated ligand such as 2-phenylpyridinato- $N, C_2'$  (ppy) and  $O\wedge O$  is a  $\beta$ -diketonate ligand. These platinum complexes have been used as phosphorescent dopants in vacuum-deposited OLEDs in conjunction with 4,4'-(carbazol-9-yl)biphenyl (CBP, **1**, Chart 1) as a host material.<sup>18</sup> A styryl derivative of acetylacetonate has been incorporated into copolymers with triphenylamine-based hole-transport monomers and oxadiazole-based electron-transport monomers;  $Pt(C\wedge N)$  building blocks were then bound to the  $O\wedge O$  ligands in the polymer, and the resulting Pt-containing copolymers were used in single-layer solution-processible near-white OLEDs.<sup>19</sup>

For some years now, we have been interested in the side-chain polymeric approach to OLEDs.<sup>12</sup> An important aspect of such work is to establish the extent to which devices based on side-chain polymers resemble or differ from vapor-deposited small-molecule devices. Here we investigate monomers and copolymers containing  $Pt(C\wedge N)(O\wedge O)$  phosphors and modified CBP as side chains, compare the photophysical properties of these monomers and polymers with those of the previously reported small-molecule species, and describe preliminary evaluation of these materials in organic light-emitting diodes with structures similar to those reported for analogous small molecules.<sup>18</sup> We have recently been interested in ring-opening metathesis polymerization (ROMP) of substituted norbornenes for side-chain polymeric OLED materials<sup>16,20</sup> and have used the same approach in the present work. In many cases, ROMP offers the possibility of obtaining polymers with narrow polydispersity indices, of obtaining well-defined block copolymers, and of incorporating a wide range of other chemical functionalities into polymers.<sup>21</sup> Second, the nonpolar poly(norbornene) backbone should have relatively little adverse effect on charge mobility in attached transport materials according to the disorder formalism of Borsenberger and Bäessler;<sup>22</sup> indeed we have measured higher hole mobilities in

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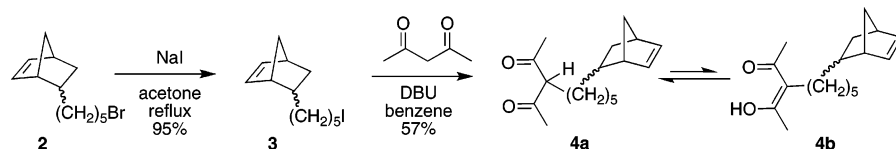
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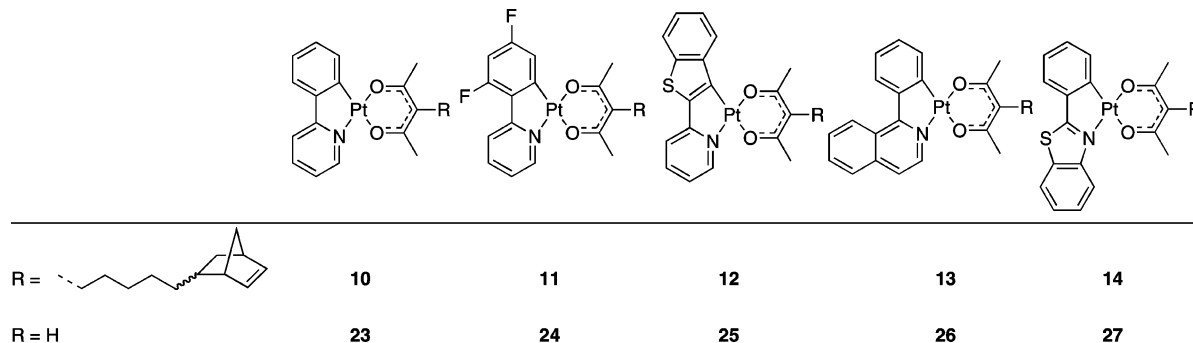
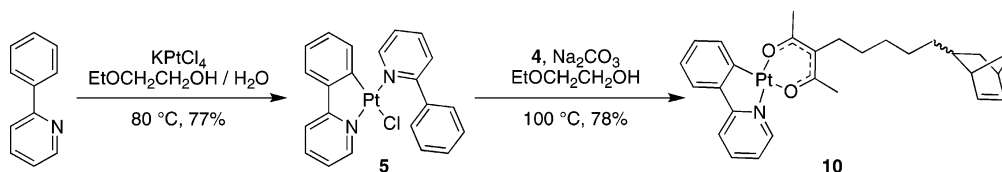
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## Scheme 1. Synthesis of 3-(5-(Bicyclo[2.2.1]hept-5-en-2-yl)pentyl)pentane-2,4-dione (4)



## Chart 2. Structures of Norbornene-Functionalized Organoplatinum Phosphors (10–14) and Small-Molecule Analogues (23–27)

Scheme 2. Synthesis of Platinum(II) (2-Phenylpyridinato-*N,C*<sup>2'</sup>)(3-(5-bicyclo[2.2.1]hept-5-en-2-yl)pentyl)pentane-2,4-dionato-*O,O* (10)

poly(norbornene)s with bis(diarylamino)fluorene side groups than for analogous poly(acrylate)s.<sup>20a</sup>

## Results and Discussion

**Synthesis of Norbornene-Substituted Acetylacetonate Ligands.** Potentially one could incorporate the norbornene moiety into a variety of cyclometalating ligands in order to prepare phosphors with different color emissions; however, a simpler way to create a library of polymerizable phosphorescent platinum complexes is to attach a norbornene moiety to the common acetylacetonate ancillary ligand in the 3-position. The reaction scheme for the preparation of norbornene-substituted acetylacetonate ligands is shown in Scheme 1. The synthesis of 5-(5-bromopentyl)bicyclo[2.2.1]hept-2-ene (**2**) was carried out according to a published procedure.<sup>23</sup> Compound **2** was converted to 5-(5-iodopentyl)bicyclo[2.2.1]hept-2-ene (**3**) by reacting with NaI in refluxing acetone and was used directly for the next step without further purification. 3-(5-(Bicyclo[2.2.1]hept-5-en-2-yl)pentyl)pentane-2,4-dione (**4**) was prepared, by analogy to a method reported by Ono et al.<sup>24</sup> for the selective monoalkylation of acetylacetone, using **3** as an alkylating agent and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base; **4** was purified by column chromatography and was obtained as a light yellow liquid. <sup>1</sup>H NMR data suggest that **4** is formed as an equilibrium mixture of its keto and enol isomers. On the basis of DEPT, COSY, and HETCOR experiments, the resonances of **4** (both keto and enol forms) in <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were assigned (see Supporting Information). The ratio of keto form to enol form at room temperature is approximately 62:38 based on integration values in the <sup>1</sup>H NMR spectrum of **4**.

**Synthesis of Norbornene Monomers Containing Platinum Complexes.** The monomers of phosphorescent cyclometalated platinum complexes of the general structure Pt(*C*^*N*)(*O*^*O*\*) {*HC*^*N* = Hppy, 2-(2,4-difluorophenyl)pyridine (H-4,6-dfppy),

2-benzo[*b*]thiophen-2-ylpyridine (Hbtp), 1-phenylisoquinoline (Hpiq), and 2-phenylbenzothiazole (Hbt) and HO^*O*^\* is 3-(5-(bicyclo[2.2.1]hept-5-en-2-yl)pentyl)pentane-2,4-dione} were prepared in a two-step procedure. The intermediate Pt complexes are mononuclear species of the general type Pt(*C*^*N*)(*HC*^*N*)(Cl) (**5**–**9**) obtained from the reaction of K<sub>2</sub>PtCl<sub>4</sub> and *HC*^*N*.<sup>25</sup> Norbornene-functionalized Pt(*C*^*N*)(*O*^*O*\*) species, **10**–**14**, shown in Chart 2 along with their nonfunctionalized analogues, **23**–**27** (*vide infra*), were obtained from the reactions of these intermediate Pt complexes with the appropriate diketone (**4** or acetylacetone) in the presence of excess Na<sub>2</sub>CO<sub>3</sub> in 2-ethoxyethanol. Scheme 2 illustrates the synthesis for the example of platinum(II) (2-phenylpyridinato-*N,C*<sup>2'</sup>)(3-(5-bicyclo[2.2.1]hept-5-en-2-yl)pentyl)pentane-2,4-dionato-*O,O* (**10**). Platinum(II) (2-(4',6'-difluorophenyl)pyridinato-*N,C*<sup>2'</sup>)(3-(5-bicyclo[2.2.1]hept-5-en-2-yl)pentyl)pentane-2,4-dionato-*O,O* (**11**), platinum(II) (2,2'-(4',5'-benzo)thienyl)pyridinato-*N,C*<sup>3'</sup>)(3-(5-bicyclo[2.2.1]hept-5-en-2-yl)pentyl)pentane-2,4-dionato-*O,O* (**12**), platinum(II) (1-phenylisoquinolinato-*N,C*<sup>2'</sup>)(3-(5-bicyclo[2.2.1]hept-5-en-2-yl)pentyl)pentane-2,4-dionato-*O,O* (**13**), and platinum(II) (2-phenylbenzothiazolato-*N,C*<sup>2'</sup>)(3-(5-bicyclo[2.2.1]hept-5-en-2-yl)pentyl)pentane-2,4-dionato-*O,O* (**14**) were prepared from their corresponding Pt intermediates using the same synthetic procedure.

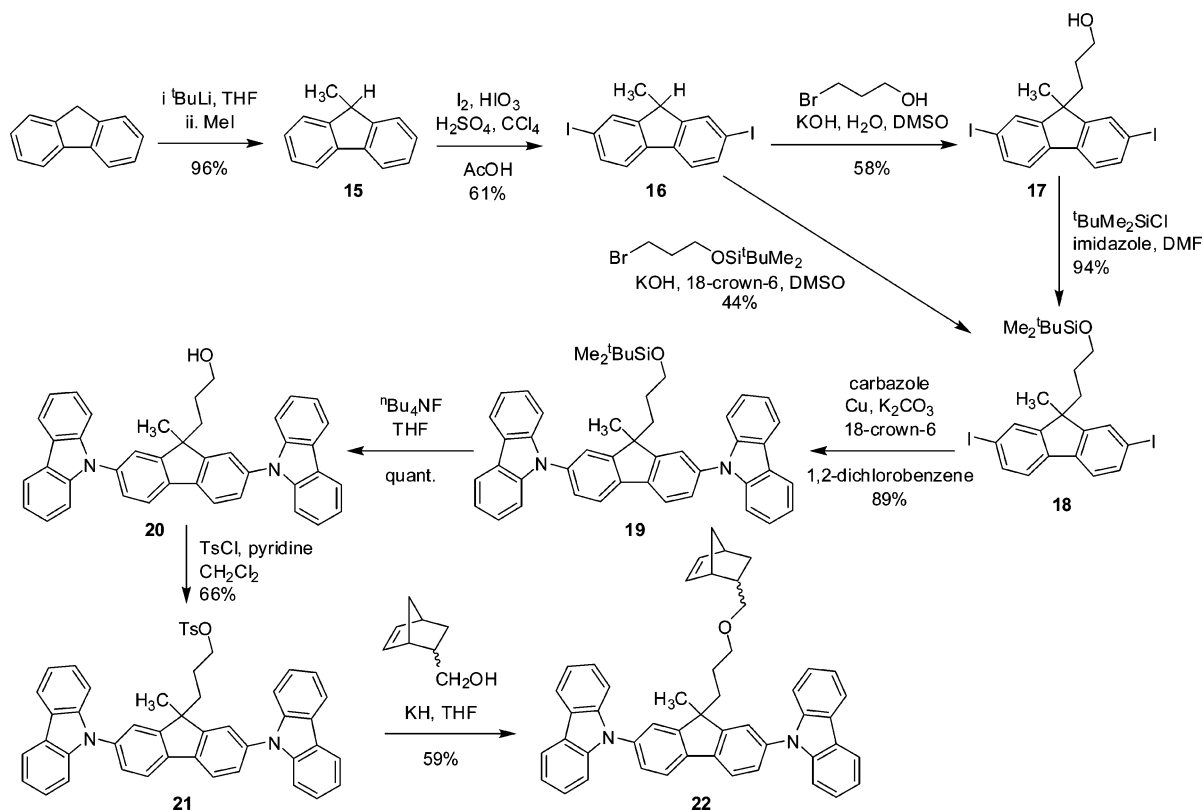
**Synthesis of Norbornene-Functionalized Host Material for Phosphors.** 4,4'-Di(carbazol-9-yl)biphenyl (CBP) has been used extensively as a host material for phosphors with different color emissions in OLEDs due to its high triplet energy of 2.56 eV (484 nm),<sup>26</sup> both host and phosphor typically being deposited

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Scheme 3. Synthesis of 9-[3-(Bicyclo[2.2.1]hept-5-en-2-ylmethoxy)propyl]-2,7-biscarbazol-9-yl-9-methyl-9H-fluorene (**22**)

together under vacuum. Previously we have compared the thermal, spectroscopic, electrochemical, and hole-mobility properties of 2,7-bis(diarylamino)-9,9-dimethylfluorenes with their 4,4'-bis(diarylamino)biphenyl analogues and their behavior in OLEDs;<sup>27</sup> we found that fluorescence spectra and quantum yields for the two classes of compounds are similar, despite significant differences in the structure of the absorption spectra. Moreover, DFT calculations suggest that 2,7-di(carbazol-9-yl)-fluorene has a triplet energy only slightly lower (0.03 eV) than that of **1**.<sup>28</sup> Therefore, due to the ease of functionalization of fluorenes at the 9-position, we chose a functionalized norbornene monomer linked to a pendant 2,7-di(carbazol-9-yl)fluorene moiety as a host material for copolymerization with our platinum phosphor monomers. The synthesis (Scheme 3) involves monomethylation of fluorene,<sup>29</sup> followed by iodination. The protected hydroxy-functionalized 2,7-diiodofluorene, **18**, was obtained by alkylation using 3-bromo-1-propanol with subsequent protection of the resulting alcohol **17** using *tert*-butyldimethylchlorosilane; alternatively **18** can also be obtained directly by alkylation of **16** with *tert*-butyldimethylsilyl-protected 3-bromo-1-propanol, although the yield is slightly reduced in comparison to the two-step procedure. The fluorene core was coupled to carbazole using a copper-mediated Ullmann reaction<sup>30</sup> with the use of a phase-transfer reagent (18-crown-6) and a weak base ( $K_2CO_3$ ) at 185–190 °C for 3 days, followed by deprotection using tetra-*n*-butylammonium fluoride in THF to give the

Table 1. Polymer Characterization Data

polymer	$M_n$	$M_w$	PDI	$T_g/^\circ C$	Grubbs cat. used
poly- <b>22</b>	29 500	67 000	2.27	190 <sup>a</sup>	second
poly- <b>22-co-10</b>	8800	26 000	2.96	182	third
poly- <b>22-co-11</b>	13 500	46 000	3.47	185	second
poly- <b>22-co-12</b>	12 000	44 000	3.59	202	second

<sup>a</sup> For comparison, the monomer **22** shows a  $T_g$  of 94 °C, with no evidence of other thermal process in the temperature range investigated (25–220 °C).

hydroxy-functionalized 2,7-di(carbazol-9-yl)fluorene, **20**, in excellent yield. Treatment of **20** with *p*-toluenesulfonyl chloride and 2.1 equiv of pyridine in  $CH_2Cl_2$  afforded the corresponding tosylate, **21**. The norbornene monomer, **22**, was prepared at ambient temperature, using excess potassium hydride to deprotonate 5-norbornene-2-methanol, and was isolated as a colorless glassy solid.

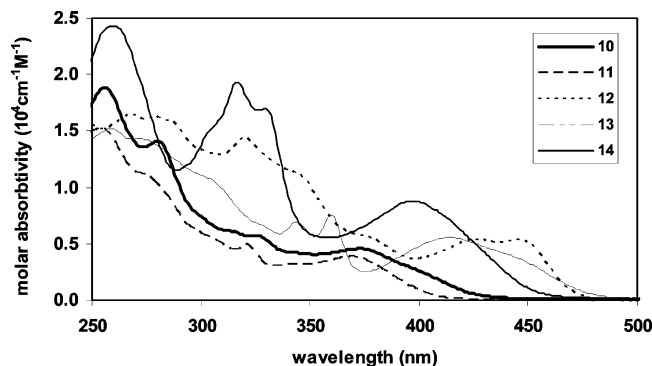
**Polymerization.** Monomers **10**, **11**, **12**, and **22** were polymerized using Grubbs' second- or third-generation ruthenium catalysts (2 mol %) in dry  $CH_2Cl_2$ . After the polymerization was complete, the reaction mixture was quenched with a few drops of ethyl vinyl ether before precipitation in cold methanol. Table 1 summarizes molecular weights determined by GPC and glass-transition temperatures ( $T_g$ ) determined by DSC for the homopolymer of **22** and random copolymers of **22** with 10 wt % of phosphor monomers: poly-**22-co-10**, poly-**22-co-11**, and poly-**22-co-12**. The synthesis of poly-**10** was also attempted using the second-generation catalyst; the resulting material was found to have a  $T_g$  of 126 °C but was too poorly soluble for characterization by GPC. The copolymers display significantly broader molecular weight distributions than the homopolymer of the host. Indeed, three different carbene <sup>1</sup>H NMR signals are seen during the formation of the copolymers, whereas only one is seen during the homopolymerization of **22**. This suggests that the ruthenium catalysts decompose at least partially during the polymerization and that the catalysts are not fully functional

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**Figure 1.** Absorption spectra of platinum complexes **10–14** in  $\text{CH}_2\text{Cl}_2$ .

**Table 2. Redox Potentials (V vs  $\text{FeCp}_2^{+/0}$ , DMF/0.1 M  $n\text{-Bu}_4\text{NPF}_6$ , 50  $\text{mV s}^{-1}$ ) of Norbornene-Substituted Platinum Complexes (**10–14**) and Their Corresponding Unsubstituted Analogues (**23–27**)**

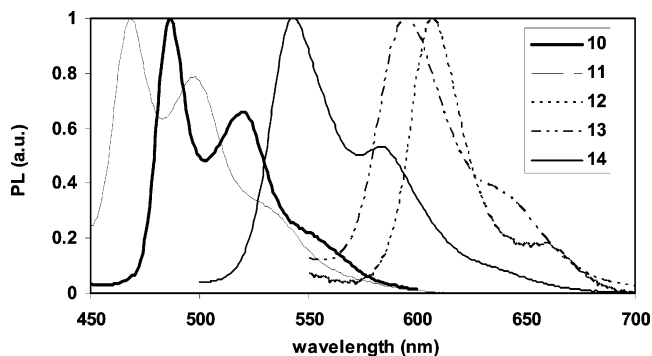
norbornene monomers			small-molecule analogues		
compound	$E_{\text{ox}}^{+/0}$	$E_{1/2}^{0/-}$	compound	$E_{\text{ox}}^{+/0}$	$E_{1/2}^{0/-}$
<b>10</b>	+0.35	-2.44	<b>23</b>	<i>a</i>	-2.39 <sup>a</sup>
<b>11</b>	+0.45	-2.27	<b>24</b>	<i>a</i>	-2.29 <sup>a</sup>
<b>12</b>	+0.45	-2.27	<b>25</b>	<i>a</i>	-2.25 <sup>a</sup>
<b>13</b>	+0.32	-2.02	<b>26</b>	+0.29	-2.00
<b>14</b>	+0.41	-2.15	<b>27</b>	+0.37	-2.13

<sup>a</sup> From ref 17, where  $E_{\text{ox}}^{+/0}$  values are not reported.

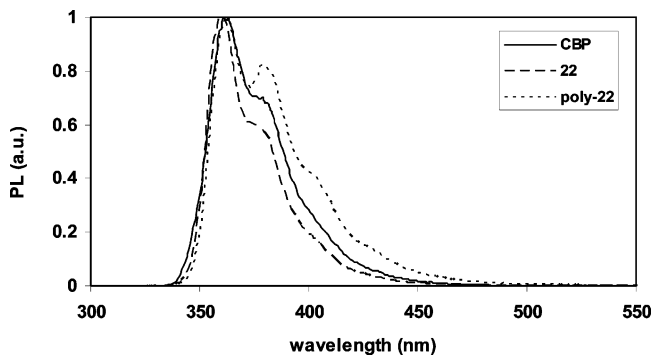
group tolerant toward the platinum complexes, perhaps due to transfer of the acetylacetonate ligand from platinum to ruthenium. While the polymerization was complete for all copolymerizations studied and polymeric material could be obtained easily, the polymerization is clearly not living.

**Electrochemistry.** The electrochemical properties of the norbornene-substituted platinum complexes (**10–14**) were studied using cyclic voltammetry; the data are compared with those for their corresponding unsubstituted Pt complexes in Table 2. In the case of **23–25**, the small-molecule analogues of **10–12**, respectively, the values in the table are taken from a previous literature report.<sup>17</sup> Small-molecule analogues of **13** and **14**, **26**<sup>25</sup> and **27**,<sup>31</sup> respectively, have recently been reported, but without electrochemical data. All complexes show a single reversible process with  $E_{1/2}$  between -2.00 and -2.44 V vs  $\text{FeCp}_2^{+/0}$ ; this can be attributed to molecular reduction, which is generally considered to be localized on the cyclometalated  $C\wedge N$  ligand. The complexes also show an irreversible, presumably metal-based, oxidation peak with  $E_{\text{ox}}$  between +0.29 and +0.45 V; oxidation of square-planar complexes is typically irreversible because of rapid solvolysis of the resultant platinum(III) species.<sup>32</sup> Table 2 clearly shows that, as expected, the electrochemical properties of these norbornene-substituted platinum complexes are not significantly affected by the incorporation of an alkylnorbornene moiety onto the backbone of the acetylacetonate ligand. The host monomer **22** has irreversible electrochemistry ( $E_{\text{ox}} = 0.58$  V vs  $\text{FeCp}_2^{+/0}$  in  $\text{CH}_2\text{Cl}_2$  at 50  $\text{mV s}^{-1}$ ) similar to that of **1**.

**Electronic Spectroscopy.** Absorption spectra of **10–14** are shown in Figure 1, and data are summarized in Table 3; the spectra are similar to those of the respective small-molecule analogues (**23–27**).<sup>17</sup> All of these complexes show visible emission under UV irradiation at room temperature, both in the



**Figure 2.** Normalized photoluminescence spectra of **10–14** in THF at room temperature.



**Figure 3.** Photoluminescence spectra of **22**, poly-**22**, and CBP (**1**) in toluene.

**Table 3. Absorption ( $\text{CH}_2\text{Cl}_2$ ) and Emission (THF, 298 K) Data for Platinum Complexes**

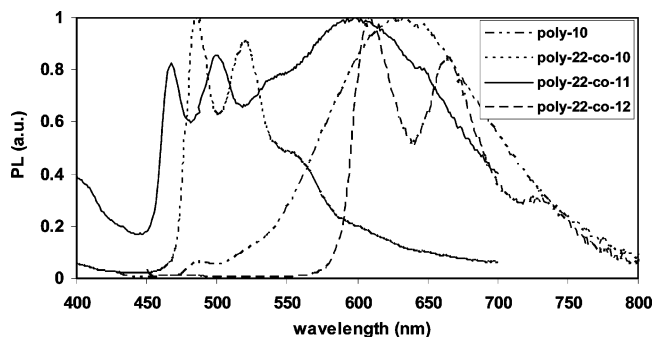
complex	$\lambda_{\text{max}}^{\text{abs}}/\text{nm}$ ( $\epsilon_{\text{max}}/10^3 \text{ cm}^{-1} \text{ M}^{-1}$ )	$\lambda_{\text{max}}^{\text{em}}/\text{nm}$
<b>10</b>	255 (54.2), 279 (40.4), 313 (sh, 17.7), 327 (sh, 16.3), 346 (sh, 12.0), 372 (13.1), 387 (sh, 10.5), 395 (sh, 8.6), 415 (sh, 3.6)	486
<b>11</b>	253 (43.3), 273 (sh, 31.8), 305 (sh, 15.7), 320 (14.1), 342 (9.1), 368 (11.1), 405 (sh, 1.8)	468
<b>12</b>	267 (30.5), 278 (30.1), 286 (29.5), 320 (26.6), 345 (sh, 20.7), 380 (sh, 10.1), 424 (10.1), 445 (10.1)	607
<b>13</b>	259 (15.2), 272 (14.3), 297 (sh, 11.3), 321 (sh, 7.3), 344 (7.0), 360 (7.6), 413 (5.5), 445 (sh, 3.7)	595
<b>14</b>	259 (24.3), 308 (sh, 15.9), 317 (19.3), 330 (17.0), 397 (8.8)	543
<b>26</b>	252 (10.1), 271 (8.9), 290 (sh, 7.6), 343 (4.1), 360 (4.6), 401 (3.2), 422 (sh, 2.2), 431 (sh, 1.9)	595
<b>27</b>	256 (13.4), 308 (sh, 8.4), 316 (10.5), 331 (9.5), 387 (4.5), 427 (sh, 1.9)	545

solid state and in dilute solution. The solution emission spectra of **10–14**, shown in Figure 2 and summarized in Table 3, are also similar to those of the corresponding small molecules.<sup>17</sup>

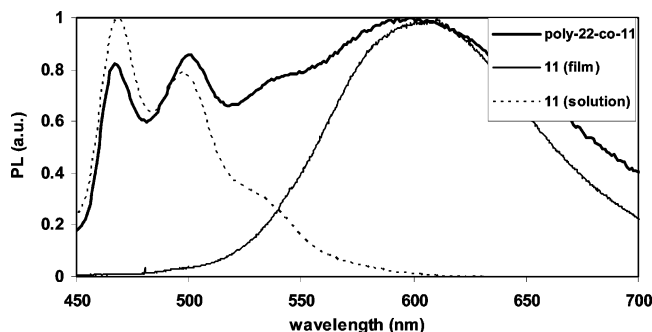
The trends observed in the absorption and fluorescence spectra of **22** or poly-**22** and **1** parallel those seen for bis-(diarylamino)fluorenes and bis-(diarylamino)biphenyls;<sup>27</sup> although the absorption spectra of the fluorene- and biphenyl-bridged compounds differ considerably, as shown in Figure 3 the fluorescence spectra are very similar. The similarity between fluorescence spectra suggests that the singlet excited states of **22** and poly-**22** have similar energy-transfer abilities as their CBP analogues. If one assumes comparable singlet–triplet splittings for the two systems, triplet energy transfer is also likely to be similar in the two classes of compounds, consistent with calculations suggesting similar triplet energies in **1** and a

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**Figure 4.** Normalized photoluminescence spectra of films of poly-10, poly-22-co-10, poly-22-co-11, and poly-22-co-12.



**Figure 5.** Photoluminescence spectra of a film of copolymer poly-22-co-11 and monomer **11** (in a thin film sample and a dilute THF solution).

fluorene-bridged analogue.<sup>28</sup> Thus, **22** and poly-**22** appear to be suitable candidates as hosts for the platinum complexes.

The square-planar geometry of platinum(II) complexes has previously been reported to promote intermolecular stacking and excimer formation, leading to substantial differences between solution and solid-state luminescence spectra.<sup>33</sup> Photoluminescence spectra of thin-film samples of our platinum materials obtained by spin-coating from  $\text{CH}_2\text{Cl}_2$  show some evidence of these aggregation effects (Figure 4). In particular, films of the homopolymer poly-**10** and of the monomer **10** show orange emission (broad peaks characterized by  $\lambda_{\text{max}}^{\text{em}} = 633$  and  $609$  nm, respectively), very different from the  $486$  nm emission observed for the monomer in solution. The copolymers poly-**22-co-10** and poly-**22-co-12**, however, show thin-film emission spectra ( $\lambda_{\text{max}}^{\text{em}} = 487$  and  $609$  nm, respectively) similar to the solution spectra of **10** and **12**, respectively, thus suggesting that copolymerization of monomers of phosphor (**10** or **12**) with **22** significantly reduces aggregation relative to that in the homopolymers or in neat films of corresponding small molecules, presumably due, at least in part, to physically separating the platinum complexes from one another. However, films of poly-**22-co-11** show near-white emission under UV irradiation; Figure 5 shows that this broad emission can be attributed to a combination of higher energy structured emission from isolated molecules, as seen for **11** in dilute solution, and a lower energy unstructured emission from aggregate states, as seen in films of **11** monomer. Thus, copolymerization of monomers of **11** and **22** fails to prevent emission from aggregate species. The result is not too surprising; moderately efficient white electroluminescence has been reported with the use of  $\text{Pt}(4,6\text{-dfppy})(\text{O}\wedge\text{O})$ , **24**, as a single emissive dopant,<sup>18</sup> balancing of molecular and aggregate emission to optimize the whiteness of

the emission in **22**-based systems has been achieved through the control of the phosphor/host ratio and the choice of host materials. The greater tendency to observe aggregate emission in **24** and **11**-based systems is perhaps due to an increase in  $\pi$ - $\pi$  stacking interactions associated with the presence of the difluorophenyl group.<sup>34</sup>

**X-ray Crystallography.** Single crystals of the complexes **10**, **12**, and **13** suitable for an X-ray diffraction study were obtained from a mixture of dichloromethane and methanol. The asymmetric unit in each case contains one molecule, the structures of which are depicted in Figure 6. The selected geometric parameters in Table 4 indicate that for all three complexes the coordination environment of platinum is slightly distorted square planar. The Pt–C bonds are shorter than the Pt–N bonds; the Pt–O(2) bonds located *trans* to Pt–C bonds are significantly elongated relative to the Pt–O(1) bonds *trans* to Pt–N bonds, consistent with the expected relative *trans* influences of aryl and pyridyl ligands.<sup>35</sup> The bond lengths are generally in the range of normally observed values for such compounds.<sup>36</sup> In the case of complex **10**, the small differences between Pt–C and Pt–N bonds and between the two Pt–O bond lengths compared to those seen in **12** and **13** suggest disorder between the pyridyl and phenyl rings of the ppy ligand; however, poor crystal quality meant we were unable to model this disorder in a satisfactory manner. The attached norbornene moieties are disordered in all three structures, at least in part due to the presence of both *exo* and *endo* isomers, and were in each case modeled using two orientations with equal occupancies.

In view of the observation of aggregate-based emission in films of platinum monomers (see above) and of recent studies emphasizing the influence of  $\pi$ -stacking on the luminescent properties of both organic and organoplatinum compounds,<sup>37</sup> we were interested in the nature of the aggregation in the crystal structures of **10**, **12**, and **13**. In all the structures under study, stacking interactions are observed between  $\pi$ -conjugated ligands of the neighboring molecules. The crystal structure of complex **10** can be described as being built up from columns in the direction of the crystallographic screw axis; in the column, molecules are related by translations along the shortest crystallographic axis (*b*-) with equal distances of  $3.43(2)$  Å between conjugated planar fragments of adjacent molecules. Figure 7 shows the crystal packing and overlap between the substituted acac ligand of one complex and the ppy ligand of its neighbor. The shortest interatomic distance is  $3.561(13)$  Å for the C(12)⋯C(1)[*x*,  $-1+y$ , *z*] atomic pair, implying weak interaction between these  $\pi$ -systems.

In the crystal structure of **12**, molecules form translational columns along the *a*-axis. In contrast to complex **10**, where acac–ppy stacking is observed, the stacking interactions in **12** are formed between the cyclometalated ligands of adjacent molecules. The interplanar distance is equal to  $3.35(2)$  Å, and the shortest interatomic distance is  $3.333(11)$  Å between C(11)

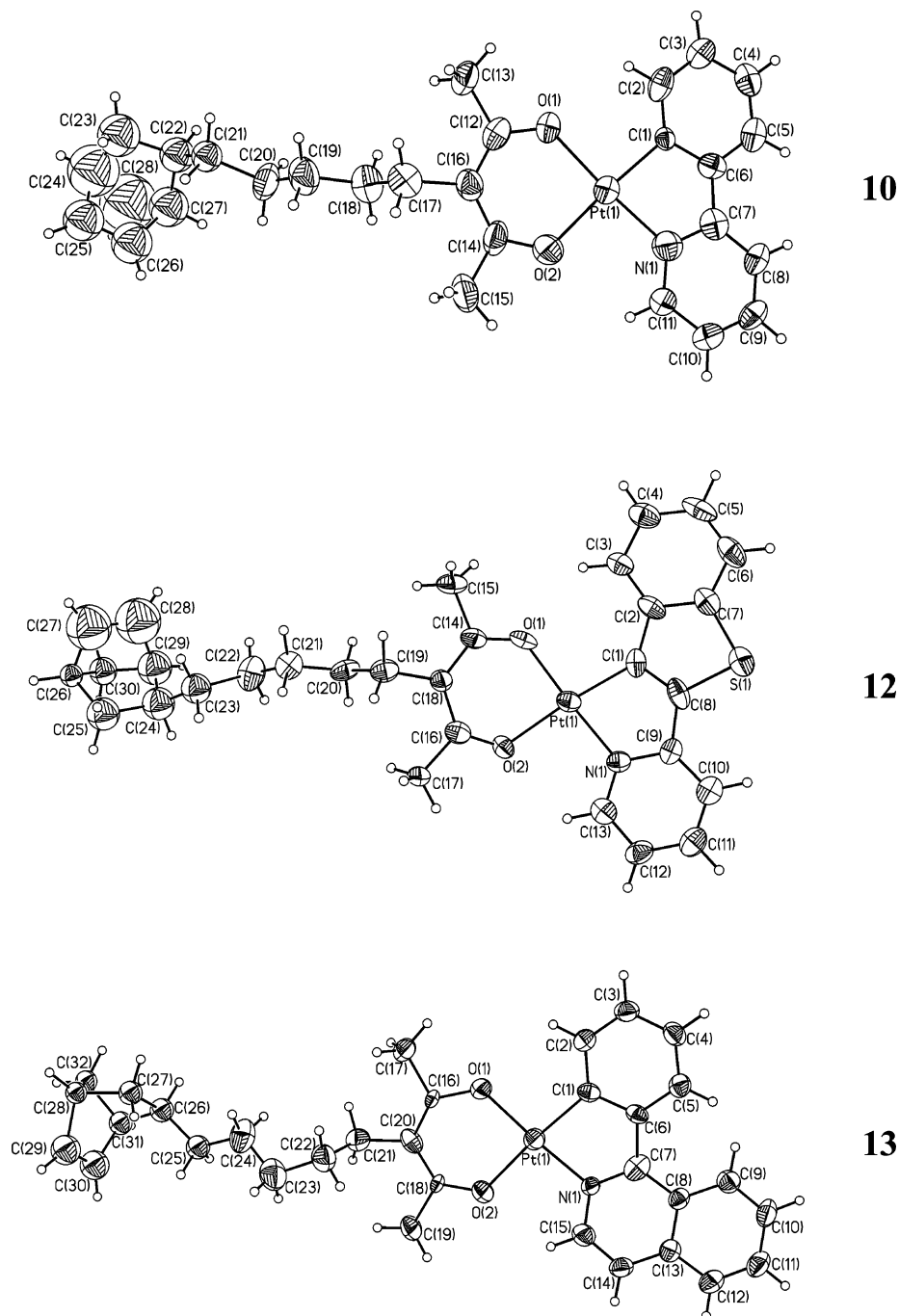
(34) For  $\pi$ - $\pi$  stacking between perfluorophenyl and phenyl groups, see: Coates, G. W.; Dunn, A. R.; Henling, L. M.; Ziller, J. W.; Lobkovsky, E. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 3641.

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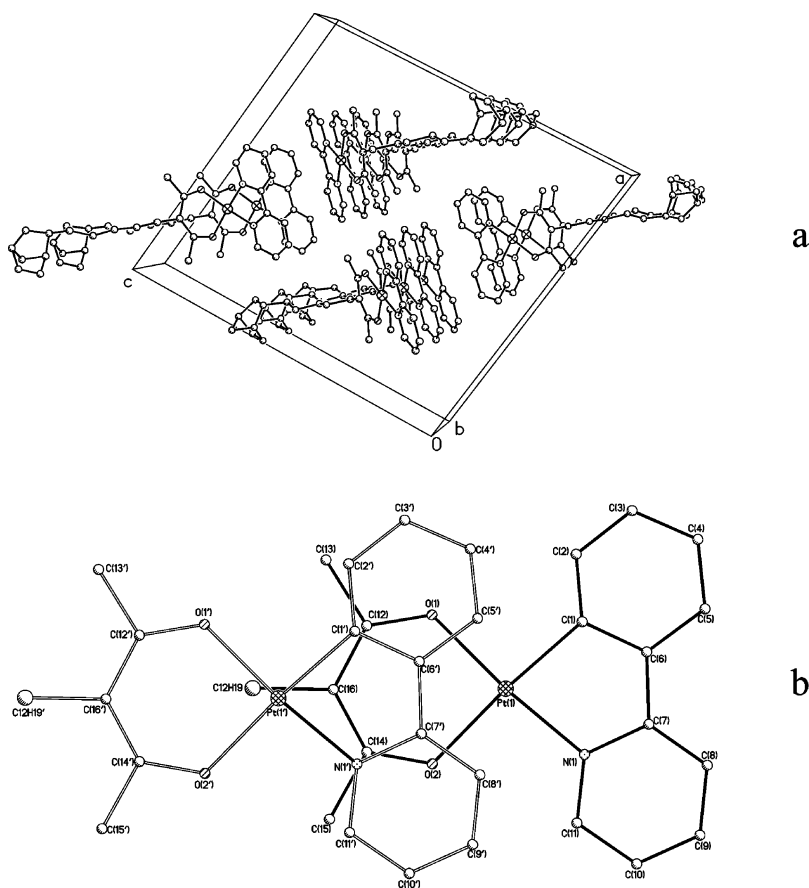
**Figure 6.** ORTEP views (50% probability) of complexes **10**, **12**, and **13**. Only one orientation of the disordered norbornene side chains is shown.

**Table 4. Selected Bond Lengths (Å) and Angles (deg) for Platinum Monomers**

	<b>10</b>	<b>12</b>	<b>13</b>
Pt(1)–C(1)	2.002(8)	1.978(7)	1.959(5)
Pt(1)–N(1)	2.020(9)	2.001(6)	1.978(4)
Pt(1)–O(1)	2.058(6)	1.972(5)	1.986(4)
Pt(1)–O(2)	2.070(7)	2.056(4)	2.061(4)
O(1)–Pt(1)–C(1)	93.5(3)	96.4(3)	95.02(18)
O(1)–Pt(1)–N(1)	174.6(3)	176.8(2)	176.08(16)
C(1)–Pt(1)–N(1)	81.4(4)	80.4(3)	81.2(2)
O(1)–Pt(1)–O(2)	90.8(3)	88.91(19)	89.73(15)
C(1)–Pt(1)–O(2)	175.0(3)	174.4(3)	175.3(2)
N(1)–Pt(1)–O(2)	94.2(3)	94.3(2)	94.01(16)

and C(2)[1+x, y, z] atoms. The overlap area (which does not involve the sulfur atom of the cyclometalated ligand) and the crystal packing are shown in Figure 8.

The structure of the columns in the crystal structure of **13** is different from those in crystals of **10** and **12**; here molecules within a column are related by the center of symmetry. The columns are parallel to the [1 1 0] crystallographic direction and are built up of stacked dimers, which are connected to each other by C–H··· $\pi$  interactions. The stacking interaction is facilitated by substantial overlap of both ligands with an interplanar distance of 3.46(2) Å (Figure 11). The shortest interatomic interaction is 3.327(10) Å between C(1) and C(15)[–x, –1–y, –z]. There is also a Pt(1)···C(7) contact of 3.434(6) Å. The interatomic distances together suggest that this complex probably has the strongest intermolecular interactions of the molecules considered here. The C–H··· $\pi$  contact is formed by the H(17b) hydrogen and  $\pi$ -system of the acac ligand. The H(17b)···M distance is 2.48 Å, the C(17)–H(17b)···M angle



**Figure 7.** Crystal packing of **10**. (a) Fragment of crystal packing as a projection onto the  $ac$  plane. (b) Stacking interaction between  $[x, y, z]$  and  $[x, -1+y, z]$  (denoted by primed atomic labels and open bond lines).

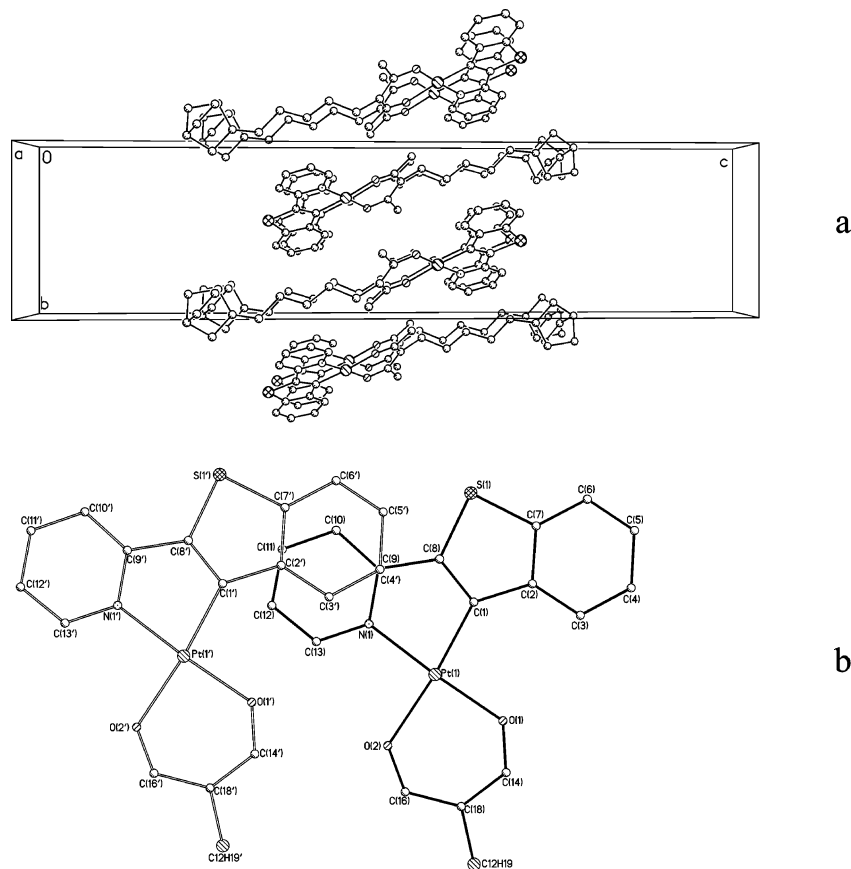
is  $142^\circ$ , and the angle between the mean plane of the ligand and the  $\text{H}(17\text{b})\cdots\text{M}$  vector is  $80^\circ$ . The crystal structure of **13** has a molecular packing of head-to-tail dimers similar to  $\text{Pt}(\text{thpy})(\text{dpm})$  { $\text{thpy} = 2$ -(2'-thienyl)pyridinato- $N, C^3$ ';  $\text{dpm} = 1,3$ -di-*tert*-butyl-1,3-propanedionato- $O, O$ '}.<sup>17</sup> The  $\pi$ -stacking interactions seen in these structures and those previously reported may be related to the origins of aggregate-based photo- and electroluminescence seen in the solid state for some of these species.

**Electroluminescence Behavior.** Multilayer OLEDs incorporating small-molecule platinum phosphors have been fabricated by Thompson and co-workers with the structure ITO/PEDOT:PSS/NPD/CBP:Pt-complex/BCP/AlQ<sub>3</sub>/LiF/Al, where ITO = indium tin oxide, PEDOT:PSS = poly(ethylenedioxythiophene)-polystyrenesulfonic acid (not used in all devices); NPD = 4,4'-bis(phenyl- $\alpha$ -naphthylamino)biphenyl; BCP = bathocuproine (2,9-dimethyl-4,7-diphenyl[1,10]phenanthroline); and AlQ<sub>3</sub> = aluminum tris(8-hydroxyquinolate).<sup>18</sup> We fabricated OLEDs in which our platinum-containing copolymers act as lumophores using similar device structures. Specifically, the photo-cross-linkable hole-transport polymer **25** (Chart 3), which we have previously reported,<sup>12d</sup> was spin-coated onto ITO and cross-linked by exposure to UV irradiation ( $\lambda_{\text{max}} \approx 310$  nm, 1 min). Onto this hole-transport layer, a platinum-containing copolymer, with the loading of the platinum complex in each copolymer being approximately 10 wt %, was then spin-coated. Finally, BCP (15 nm), AlQ<sub>3</sub> (20 nm), and LiF (1 nm) were evaporated on top of the polymers, followed by the metal cathode (Al). For comparison we also fabricated devices in which the phosphor copolymer layer was replaced with a spin-coated layer of poly-**22** and small-molecule platinum complexes (at 10 wt %). The electroluminescence (EL) spectra of the poly-

**22**/small-molecule and the corresponding copolymer devices are shown in Figures 10 and 11, respectively. The devices have broad EL spectra throughout the visible, similar to those previously seen in vapor-deposited OLEDs and attributed to a combination of emissions from aggregates or excimers and from monomers. Typically, the appearance of these EL spectra depends on the concentration of phosphor in the host and on the driving voltage of the device.<sup>16b</sup> Our EL spectra differ to varying degrees from the solid-state PL spectra of the copolymers. The EL spectra of the copolymer and the corresponding poly-**22**/small-molecule devices are broadly similar in each case, but there are significant differences in the detailed structure of the spectra seen in the comparisons of poly-**22**-co-**10** vs poly-**22**/**23** and of poly-**22**-co-**11** vs poly-**22**/**24**. In both types of devices, the peak at 440 nm can presumably be attributed to fluorescence from the photo-cross-linkable TPD-based polymer **28**,<sup>38</sup> by analogy with similar emission observed by Thompson et al. and attributed to emission from the NPD hole-transport layer used, which results from incomplete electron-hole recombination in the host/phosphor layer.<sup>18</sup> However, the relative contribution of this luminescence to the total emission appears to be reduced in the copolymer devices, at least in the poly-**22**-co-**11** vs poly-**22**/**24** comparison. The results clearly indicate the side-chain polymer approach to OLEDs can be successfully adapted to incorporate phosphorescent lumophores. However, while the details of the observed aggregate emissions change somewhat depending on whether copolymers or small molecules are used in conjunction with the polymer host, the copolymer approach evidently does not disrupt the aggregation of platinum(II) 2-(4',6'-difluorophenyl)pyridinato- $N, C^2$ ' com-

(38) The solid-state PL spectrum of **28** shows emission  $\lambda_{\text{max}}$  of 435 nm.





**Figure 8.** Crystal packing of **12**. (a) Fragment of crystal packing as a projection onto the *bc* plane. (b) Stacking interaction between  $[x, y, z]$  and  $[1+x, y, z]$  (denoted by primed atomic labels and open bond lines).

plexes sufficiently to enable simple blue phosphorescence to be achieved using poly-**22-co-11**.

### Conclusions

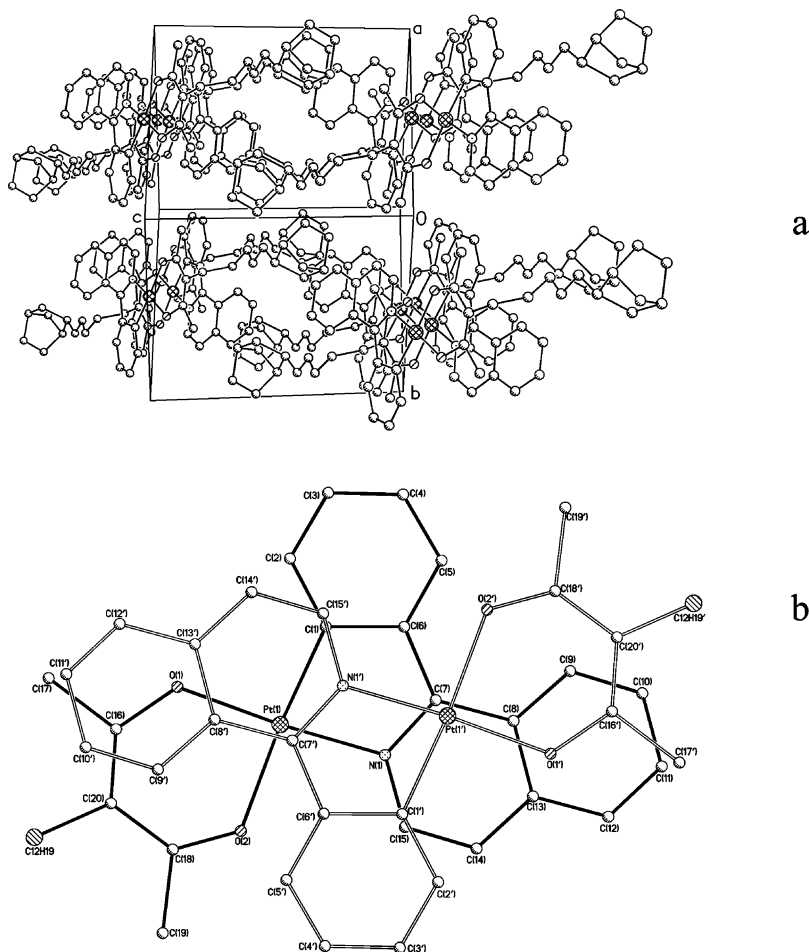
We have described the synthesis of a series of new phosphorescent Pt complexes of the form  $\text{Pt}(\text{C}\wedge\text{N})(\text{O}\wedge\text{O}^*)$ , where  $\text{C}\wedge\text{N}$  is a cyclometalated aryl pyridine and  $\text{O}\wedge\text{O}^*$  is a norbornene-functionalized acetylacetonate ligand, which show solution absorption and luminescence spectra and electrochemical behavior very similar to analogues without the norbornene group. We have also synthesized a polymerizable host material; this compound is based on a norbornene-functionalized analogue of *N,N'*-dicarbazolyl-4,4'-biphenyl, which is widely used as a host material for platinum- and iridium-based phosphors since it is capable of transferring both singlet and triplet excitation to a wide variety of phosphorescent dopants. Copolymers of our phosphor monomers and the host monomer can be synthesized using Grubbs' ruthenium catalysts; however, the platinum complexes appear to interfere with the polymerization process and broad molecular-weight distributions are obtained. Nevertheless, the copolymers can be used to fabricate functioning OLEDs, thus demonstrating extension of the possibility of phosphorescent multilayer devices based on side-chain polymers. OLED data suggest that aggregate-based emission in these copolymers has comparable importance to that in vapor-deposited devices based on small host and phosphor molecules, with aggregate emission being particularly important for phosphors with the shortest wavelength emission. Although the copolymer approach seems to provide no clear advantage in controlling aggregate emission, it may be advantageous when solution processibility is desirable. Moreover, the host monomer

may be used in other multilayer polymeric phosphorescent OLEDs, for example, copolymerized with recently described iridium norbornene monomers.<sup>16</sup>

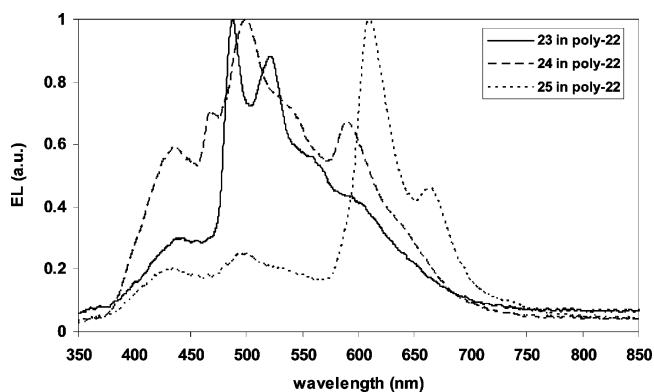
### Experimental Section

**General Considerations.** All experiments with air- and moisture-sensitive intermediates and compounds were carried out under an inert atmosphere of dry nitrogen using standard Schlenk techniques.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra (solution) were recorded on Varian Mercury-300 spectrometers and referenced to residual proton solvent signals. Elemental analyses were performed at Atlantic Microlab, Inc. High-resolution mass spectral analyses were performed by the Bioanalytical Mass Spectrometry Facility at Georgia Institute of Technology. Electrochemical measurements were carried out under dinitrogen for deoxygenated DMF solutions of tetra-*n*-butylammonium hexafluorophosphate (0.1 M) using a computer-controlled BAS 100B electrochemical analyzer, a glassy-carbon working electrode, a platinum-wire auxiliary electrode, and an Ag wire anodized with AgCl as a pseudoreference electrode. Potentials were referenced to the ferrocenium/ferrocene ( $\text{FeCp}_2^{+/0}$ ) couple using ferrocene as an internal standard. 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 Shimadzu FP-5301PC spectrofluorometer or a Fluorolog III ISA spectrofluorometer.

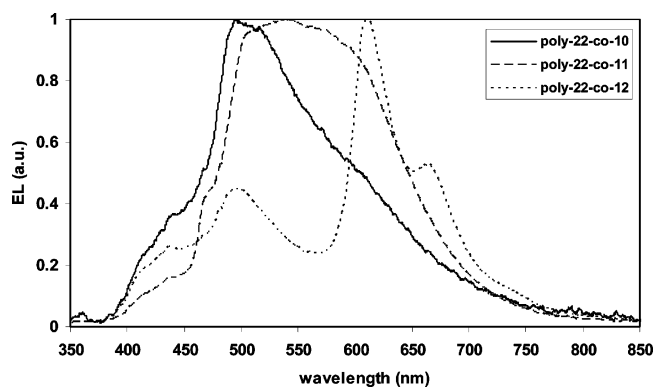
$\text{K}_2\text{PtCl}_4$  (Strem), 2-phenylpyridine (Hppy), 2-phenylbenzothiazole (Hbt), 2,4-pentanedione, potassium hydride, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), sodium carbonate, iodine, iodic acid, 3-bromo-1-propanol, fluorene, sodium thiosulfate, carbon tetrachloride, *tert*-butyldimethylchlorosilane, imidazole, *p*-toluenesulfonyl chloride, tetrabutylammonium fluoride (TBAF), 18-crown-6, potassium carbonate, sodium iodide, anhydrous 1,2-dichloroben-



**Figure 9.** Crystal packing of **13**. (a) Fragment of crystal packing as a projection onto the (1 1 0) plane. (b) Stacking interaction between  $[x, y, z]$  and  $[-x, -1-y, -z]$  (denoted by primed atomic labels and open bond lines).



**Figure 10.** Electroluminescence spectra for devices with structure ITO/cross-linked-**28**/poly-**22**:10%phosphor/BCP/Alq<sub>3</sub>/LiF/Al at an applied voltage of 12 V.



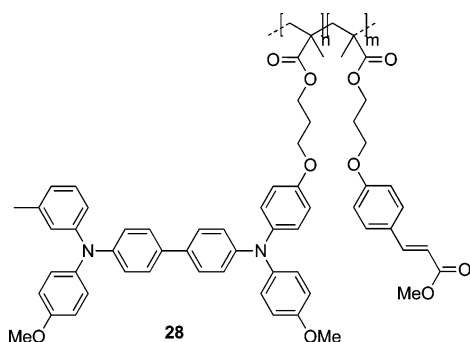
**Figure 11.** Electroluminescence spectra for devices with structure ITO/cross-linked-**28**/poly-**22-co-10**, poly-**22-co-11**, or poly-**22-co-12**/BCP/Alq<sub>3</sub>/LiF/Al at an applied voltage of 12 V.

zene, and 2-ethoxyethanol (Aldrich) were used as received without further purification. H-4,6-dfppy, Hbtp, and Hpiq were prepared via the Suzuki coupling reactions of commercially available boronic acids with 2-bromopyridine or 1-chloroisoquinoline. Carbazole was recrystallized from ethanol. **2**,<sup>23</sup> **5**–**8**,<sup>25</sup> **23**–**25**,<sup>17</sup> and **28**<sup>12d</sup> were prepared according to the literature.

**5-(5-Iodopentyl)bicyclo[2.2.1]hept-2-ene (mixture of endo and exo isomers) (3).** **2** (5.0 g, 20.6 mmol) and NaI (6.16 g, 41.1 mmol) were refluxed in acetone at 80 °C overnight. Volatiles were removed under reduced pressure. H<sub>2</sub>O was added to the residue, and the mixture was extracted with diethyl ether. The organic layer was dried over anhydrous MgSO<sub>4</sub>, and volatiles were removed under reduced pressure to give a yellowish oil (5.70 g, 95%). *Endo*

isomer: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 6.09 (dd, *J* = 5.5 Hz, 3.0 Hz, 1H), 5.88 (dd, *J* = 5.8 Hz, 3.3 Hz, 1H), 3.16 (t, *J* = 7.1 Hz, 2H), 2.72 (m, 2H), 0.42–2.00 (m, 13H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>) δ 136.85, 132.21, 49.59, 45.41, 42.54, 38.69, 34.61, 33.60, 32.45, 30.81, 27.62, 7.48; HRMS-EI (*m/z*) [M]<sup>+</sup> calcd for C<sub>12</sub>H<sub>19</sub>I, 290.05315; found, 290.05315.

**3-(5-(Bicyclo[2.2.1]hept-5-en-2-yl)pentyl)pentane-2,4-dione (4).** **5-(5-Iodopentyl)bicyclo[2.2.1]hept-2-ene (3)** (15.0 g, 51.7 mmol) was added to a solution of 2,4-pentanedione (5.18 g, 51.7 mmol) and DBU (7.87 g, 51.7 mmol) in C<sub>6</sub>H<sub>6</sub> (120 mL). The reaction mixture was stirred at room temperature overnight, after which the DBU·HI salt was filtered and the filtrate was concentrated under reduced pressure. The crude product was purified by column

**Chart 3. Structure of Photo-cross-linkable Hole-Transport Polymer 28;  $n/m = \text{ca. } 4$** 

chromatography (silica gel, hexanes/dichloromethane = 1:3 (v/v)) to give a light yellow liquid (7.75 g, 57%). *Endo* isomer (keto form):  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  6.05–6.08 (m, 1H), 5.84–5.87 (m, 1H), 3.56 (t,  $J = 7.4$  Hz, 1H), 2.70 (br, 2H), 2.13 (s, 6H), 0.40–2.00 (m, 15H). (Enol form):  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  16.63 (s, 1H), 6.05–6.08 (m, 1H), 5.84–5.87 (m, 1H), 2.70 (br, 2H), 2.09 (s, 6H), 0.40–2.00 (m, 14H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  204.31, 190.71, 136.77, 132.19, 110.50, 69.05, 49.56, 45.41, 45.38, 42.51, 38.75, 38.69, 34.82, 34.67, 32.45, 32.42, 30.72, 29.92, 29.72, 29.10, 28.50, 28.38, 28.35, 27.65, 27.62, 22.93. HRMS-EI ( $m/z$ ):  $[\text{M}]^+$  calcd for  $\text{C}_{17}\text{H}_{26}\text{O}_2$ , 262.19328; found, 262.19483. Anal. Calcd for  $\text{C}_{17}\text{H}_{26}\text{O}_2$ : C, 77.82; H, 9.99. Found: C, 77.26; H, 9.90.

**Platinum(II) (2-Phenylpyridinato- $N, C^2$ ')(3-(5-(bicyclo[2.2.1]hept-5-en-2-yl)pentyl)pentane-2,4-dionato- $O, O$ ')(10).** A mixture of **5** (1.0 g, 1.85 mmol), **4** (1.02 g, 3.9 mmol), and  $\text{Na}_2\text{CO}_3$  (1.38 g, 13.0 mmol) in 2-ethoxyethanol (100 mL) was heated at 100 °C overnight under a  $\text{N}_2$  atmosphere. The reaction mixture was allowed to cool to room temperature, and  $\text{H}_2\text{O}$  was added. The mixture was extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was washed with  $\text{H}_2\text{O}$  and dried over anhydrous  $\text{MgSO}_4$ . Volatiles were removed under reduced pressure to give a brown oil. The crude product was purified by column chromatography (silica gel, hexanes/dichloromethane = 1:1 (v/v)) to give a yellow crystalline solid (0.88 g, 78%), mp 160–162 °C.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.93 (dd,  $J = 5.8$  Hz, 0.8 Hz, 1H), 7.76 (td,  $J = 7.4$  Hz, 1.6 Hz, 1H), 7.60 (dd,  $J = 7.7$  Hz, 1.1 Hz, 1H), 7.56 (d,  $J = 7.7$  Hz, 1H), 7.41 (dd,  $J = 7.7$  Hz, 1.1 Hz, 1H), 7.18 (td,  $J = 7.4$  Hz, 1.4 Hz, 1H), 7.02–7.08 (m, 2H), 6.09 (dd,  $J = 5.8$  Hz, 3.0 Hz, 1H), 5.90 (dd,  $J = 5.5$  Hz, 2.7 Hz, 1H), 2.74 (br, 2H), 2.26–2.32 (m, 2H), 2.114 (s, 3H), 2.105 (s, 3H), 0.98–2.02 (m, 12H), 0.44–0.50 (m, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  184.42, 182.19, 168.29, 146.91, 144.61, 139.96, 137.84, 136.79, 132.30, 130.55, 129.08, 123.28, 122.87, 120.97, 118.23, 111.94, 49.60, 45.46, 42.57, 38.81, 34.94, 32.51, 31.15, 31.05, 30.25, 28.58, 27.87, 26.99. HRMS-EI ( $m/z$ ):  $[\text{M}]^+$  calcd for  $\text{C}_{28}\text{H}_{33}\text{NO}_2\text{Pt}$ , 609.21381; found, 609.21258. Anal. Calcd for  $\text{C}_{28}\text{H}_{33}\text{NO}_2\text{Pt}$ : C, 55.07; H, 5.45; N, 2.29. Found: C, 55.10; H, 5.40; N, 2.27.

**Platinum(II) (2-(4',6'-Difluorophenyl)pyridinato- $N, C^2$ ')(3-(5-(bicyclo[2.2.1]hept-5-en-2-yl)pentyl)pentane-2,4-dionato- $O, O$ ')(11).** A mixture of **6** (1.0 g, 1.63 mmol), **4** (0.935 g, 3.6 mmol), and  $\text{Na}_2\text{CO}_3$  (1.26 g, 11.9 mmol) in 2-ethoxyethanol (60 mL) was heated at 100 °C overnight under a  $\text{N}_2$  atmosphere. The reaction mixture was allowed to cool to room temperature, and  $\text{H}_2\text{O}$  was added. The mixture was extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was washed with  $\text{H}_2\text{O}$  and dried over anhydrous  $\text{MgSO}_4$ . Volatiles were removed under reduced pressure. The crude product was purified by column chromatography (silica gel, dichloromethane as eluting solvent) to give a yellow-brown solid (0.81 g, 77%), mp 148–149 °C.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.91 (d,  $J = 5.5$  Hz, 1H), 7.90 (d,  $J = 8.0$  Hz, 1H), 7.77 (t,  $J = 7.7$  Hz, 1H), 7.03–7.09 (m, 2H), 6.49–6.56 (m, 1H), 6.09 (dd,  $J = 5.5$  Hz, 3.0 Hz, 1H), 5.90 (dd,

$J = 5.5$  Hz, 2.7 Hz, 1H), 2.73 (br, 2H), 2.24–2.30 (m, 2H), 2.11 (s, 3H), 2.10 (s, 3H), 1.00–2.01 (m, 12H), 0.44–0.50 (m, 1H). HRMS-EI ( $m/z$ ):  $[\text{M}]^+$  calcd for  $\text{C}_{28}\text{H}_{31}\text{NO}_2\text{PtF}_2$ , 646.19707; found, 646.19358. Anal. Calcd for  $\text{C}_{28}\text{H}_{31}\text{NO}_2\text{PtF}_2$ : C, 52.01; H, 4.83; N, 2.17. Found: C, 52.28; H, 4.87; N, 2.05.

**Platinum(II) (2,2'-(4',5'-Benzo(thienyl)pyridinato- $N, C^3$ ')(3-(5-(bicyclo[2.2.1]hept-5-en-2-yl)pentyl)pentane-2,4-dionato- $O, O$ ')(12).** A mixture of **7** (1.0 g, 1.53 mmol), **4** (0.89 g, 3.4 mmol), and  $\text{Na}_2\text{CO}_3$  (1.20 g, 11.3 mmol) in 2-ethoxyethanol (60 mL) was heated at 100 °C overnight under a  $\text{N}_2$  atmosphere. The reaction mixture was allowed to cool to room temperature, and  $\text{H}_2\text{O}$  was added. The mixture was extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was washed with  $\text{H}_2\text{O}$  and dried over anhydrous  $\text{MgSO}_4$ . Volatiles were removed under reduced pressure. The crude product was purified by column chromatography (silica gel, dichloromethane as eluting solvent) to give an orange-brown solid (0.76 g, 75%), mp 184–185 °C.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.73–8.87 (m, 2H), 7.76–7.80 (m, 1H), 7.62 (t,  $J = 7.7$  Hz, 1H), 7.28–7.35 (m, 2H), 7.23 (d,  $J = 8.2$  Hz, 1H), 6.86 (t,  $J = 6.3$  Hz, 1H), 6.10 (dd,  $J = 5.8$  Hz, 3.0 Hz, 1H), 5.91 (dd,  $J = 5.5$  Hz, 2.7 Hz, 1H), 2.74 (br, 2H), 2.26–2.32 (m, 2H), 2.15 (s, 3H), 2.10 (s, 3H), 1.00–2.02 (m, 12H), 0.45–0.51 (m, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  183.66, 181.31, 164.48, 146.55, 145.35, 142.21, 140.27, 138.37, 138.07, 136.81, 132.28, 126.57, 125.18, 123.92, 122.20, 118.56, 117.97, 111.94, 49.60, 45.46, 42.56, 38.80, 34.92, 32.51, 31.07, 30.87, 30.23, 28.55, 27.55, 25.85. HRMS-EI ( $m/z$ ):  $[\text{M}]^+$  calcd for  $\text{C}_{30}\text{H}_{33}\text{NO}_2\text{PtS}$ , 666.18799; found, 666.18380. Anal. Calcd for  $\text{C}_{30}\text{H}_{33}\text{NO}_2\text{PtS}$ : C, 54.04; H, 4.99; N, 2.10. Found: C, 54.08; H, 5.00; N, 2.01.

**Platinum(II) (1-Phenyl-isoquinolinato- $N, C^2$ ')(3-(5-(bicyclo[2.2.1]hept-5-en-2-yl)pentyl)pentane-2,4-dionato- $O, O$ ')(13).** A mixture of **8** (0.4 g, 0.62 mmol), **4** (0.33 g, 1.2 mmol), and  $\text{Na}_2\text{CO}_3$  (0.66 g, 6.2 mmol) in 2-ethoxyethanol (15 mL) was heated at 100 °C overnight under a  $\text{N}_2$  atmosphere. The reaction was allowed to cool to room temperature, and  $\text{H}_2\text{O}$  was added. The mixture was extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was washed with  $\text{H}_2\text{O}$  and dried over anhydrous  $\text{MgSO}_4$ . Volatiles were removed under reduced pressure. The crude product was purified by column chromatography (silica gel, dichloromethane as eluting solvent) to give an orange-red solid. The product was recrystallized from a dichloromethane/methanol solvent mixture to give red crystals (82 mg, 20%).  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.92 (d,  $J = 6.6$  Hz, 1H), 8.87 (d,  $J = 8.5$  Hz, 1H), 8.08 (d,  $J = 7.7$  Hz, 1H), 7.60–7.82 (m, 4H), 7.39 (d,  $J = 6.6$  Hz, 1H), 7.22 (td,  $J = 7.4$  Hz, 1.4 Hz, 1H), 7.14 (td,  $J = 7.4$  Hz, 1.4 Hz, 1H), 6.09 (dd,  $J = 5.5$  Hz, 3.0 Hz, 1H), 5.90 (dd,  $J = 5.5$  Hz, 2.7 Hz, 1H), 2.74 (br s, 2H), 2.31 (m, 2H), 2.15 (s, 3H), 2.13 (s, 3H), 1.91–2.02 (m, 1H), 1.78–1.86 (m, 1H), 1.06–1.37 (m, 10H), 0.44–0.50 (m, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  184.71, 182.36, 168.59, 146.25, 142.68, 139.07, 137.23, 136.81, 132.31, 130.93, 130.60, 129.23, 128.35, 128.09, 127.39, 126.09, 125.92, 122.99, 119.38, 112.02, 49.62, 45.49, 42.59, 38.83, 34.96, 32.53, 31.16, 31.01, 30.26, 28.60, 27.91, 27.00. HRMS-EI ( $m/z$ ):  $[\text{M}]^+$  calcd for  $\text{C}_{32}\text{H}_{35}\text{NO}_2\text{Pt}$ , 660.23156; found, 660.23283. Anal. Calcd for  $\text{C}_{32}\text{H}_{35}\text{NO}_2\text{Pt}$ : C, 58.17; H, 5.34; N, 2.12. Found: C, 57.81; H, 5.31; N, 2.13.

**Platinum(II) (2-Phenylbenzothiazolato- $N, C^2$ ')(3-(5-(bicyclo[2.2.1]hept-5-en-2-yl)pentyl)pentane-2,4-dionato- $O, O$ ')(14).** **9** was prepared from  $\text{K}_2\text{PtCl}_4$  and 2-phenylbenzothiazole (Hbt) in a 3:1 (v/v) mixture of 2-ethoxyethanol and  $\text{H}_2\text{O}$  at 80 °C. However, poor solubility of **9** prevented its further purification. Therefore, crude **9** was used directly in the following step. A mixture of **9** (1.0 g, 1.53 mmol), **4** (0.885 g, 3.37 mmol), and  $\text{Na}_2\text{CO}_3$  (1.19 g, 11.2 mmol) in 2-ethoxyethanol (20 mL) was heated at 100 °C for 1 day under a  $\text{N}_2$  atmosphere. The reaction mixture was allowed to cool to room temperature, and  $\text{H}_2\text{O}$  was added. The mixture was extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was washed with  $\text{H}_2\text{O}$  and dried over anhydrous  $\text{MgSO}_4$ . Volatiles were removed under

reduced pressure. The crude product was purified by column chromatography (silica gel, dichloromethane as eluting solvent) to give a yellow solid. The product was recrystallized twice from a dichloromethane/methanol solvent mixture to give a yellow solid (0.17 g, 17% overall yield for two steps).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.16 (d,  $J = 8.2$  Hz, 1H), 7.77 (d,  $J = 8.0$  Hz, 1H), 7.69 (d,  $J = 7.7$  Hz, 1H), 7.53 (ddd,  $J = 8.2$  Hz, 7.1 Hz, 1.1 Hz, 1H), 7.46 (dd,  $J = 7.7$  Hz, 1.1 Hz, 1H), 7.38 (m, 1H), 7.18 (td,  $J = 7.4$  Hz, 1.4 Hz, 1H), 7.07 (td,  $J = 7.7$  Hz, 1.4 Hz, 1H), 6.09 (dd,  $J = 5.8$  Hz, 3.0 Hz, 1H), 5.91 (dd,  $J = 5.8$  Hz, 3.0 Hz, 1H), 2.74 (br, 2H), 2.29–2.34 (m, 2H), 2.18 (s, 3H), 2.12 (s, 3H), 1.77–2.02 (m, 2H), 1.00–1.05 (m, 10H), 0.45–0.51 (m, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  183.78, 181.64, 181.48, 150.66, 140.87, 139.43, 136.82, 132.30, 130.69, 130.10, 129.99, 127.26, 125.10, 124.50, 123.43, 121.91, 120.50, 111.64, 49.62, 45.49, 42.59, 38.83, 34.94, 32.53, 31.15, 30.86, 30.25, 28.60, 27.32, 26.76. HRMS-EI ( $m/z$ ):  $[\text{M}]^+$  calcd for  $\text{C}_{30}\text{H}_{33}\text{NO}_2\text{PtS}$ , 666.18799; found, 666.18721. Anal. Calcd for  $\text{C}_{30}\text{H}_{33}\text{NO}_2\text{PtS}$ : C, 54.04; H, 4.99; N, 2.10; S, 4.81. Found: C, 53.87; H, 4.91; N, 2.31; S, 4.90.

**9-Methyl-9H-fluorene (15).**<sup>29</sup> A solution of fluorene (20.0 g, 0.12 mol) in dry THF (250 mL) was allowed to cool to  $-78$  °C.  $n\text{-BuLi}$  (48.1 mL of 2.5 M solution in hexanes, 0.12 mmol) was added. The reaction mixture was stirred at  $-78$  °C for 30 min. Methyl iodide (17.08 g, 0.12 mol) in dry THF (40 mL) was added at  $-78$  °C. The resulting mixture was stirred at  $-78$  °C for 2 h, slowly warmed to room temperature, and stirred at room temperature overnight. The reaction mixture was neutralized with a saturated aqueous  $\text{NH}_4\text{Cl}$  solution. The mixture was extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was washed with  $\text{H}_2\text{O}$  and brine and dried over anhydrous  $\text{MgSO}_4$ . Volatiles were removed under reduced pressure. The crude product was purified by column chromatography (silica gel, hexanes as eluting solvent) to give a colorless semisolid (20.8 g, 96%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.74–7.78 (m, 2H), 7.49–7.54 (m, 2H), 7.28–7.40 (m, 4H), 3.95 (q,  $J = 7.4$  Hz, 1H), 1.53 (d,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  148.83, 140.37, 126.82, 123.90, 119.74, 42.47, 18.27.

**2,7-Diiodo-9-methyl-9H-fluorene (16).** A solution of **15** (9.24 g, 51.3 mmol), iodine (9.58 g, 37.7 mmol), iodic acid (4.22 g, 24 mol), concentrated  $\text{H}_2\text{SO}_4$  (4 mL), and  $\text{CCl}_4$  (6 mL) in acetic acid (80 mL) was heated at 80 °C overnight. The resulting precipitate was collected by vacuum filtration and dissolved in  $\text{CH}_2\text{Cl}_2$ . The organic layer was washed with aqueous sodium thiosulfate (0.1 M) solution and dried over anhydrous  $\text{MgSO}_4$ . Volatiles were removed under reduced pressure. The crude product was purified by column chromatography (silica gel, hexanes as eluting solvent) to give a yellow solid (13.53 g, 61%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.80 (dd,  $J = 1.6$  Hz, 0.8 Hz, 2H), 7.66 (ddd,  $J = 8.0$  Hz, 1.6 Hz, 0.8 Hz, 2H), 7.43 (d,  $J = 8.0$  Hz, 2H), 3.86 (q,  $J = 7.4$  Hz, 1H), 1.46 (d,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.41, 139.04, 136.02, 133.18, 121.50, 92.73, 42.23, 17.94. HRMS-EI ( $m/z$ ):  $[\text{M}]^+$  calcd for  $\text{C}_{14}\text{H}_{10}\text{I}_2$ , 431.88720; found, 431.88551. Anal. Calcd for  $\text{C}_{14}\text{H}_{10}\text{I}_2$ : C, 38.92; H, 2.33. Found: C, 39.24; H, 2.33.

**3-(2,7-Diiodo-9-methyl-9H-fluorene-9-yl)propan-1-ol (17).** A mixture of **16** (18.6 g, 43.1 mmol), 3-bromo-1-propanol (7.18 g, 51.7 mmol), potassium hydroxide (2.90 g, 51.7 mmol),  $\text{H}_2\text{O}$  (4 mL), DMSO (100 mL), and 18-crown-6 (1.14 g, 4.3 mmol) was stirred at room temperature overnight. The reaction mixture was extracted with  $\text{CH}_2\text{Cl}_2$ , and the organic layer was washed with saturated NaCl aqueous solution and water. The organic layer was dried over  $\text{MgSO}_4$ , after which volatiles were removed under reduced pressure. The product was purified by column chromatography (silica gel, hexanes/dichloromethane = 1:1, then dichloromethane as eluting solvent) to give a pale yellow solid (12.15 g, 58%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.68 (d,  $J = 1.1$  Hz, 2H), 7.64 (dd,  $J = 8.0$  Hz, 1.6 Hz, 2H), 7.40 (d,  $J = 8.0$  Hz, 2H), 3.39 (t,  $J = 6.6$  Hz, 2H),

1.99 (m, 2H), 1.44 (s, 3H), 1.39 (s, 1H), 0.88 (m, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  153.14, 138.66, 136.18, 131.89, 121.63, 93.20, 62.79, 50.79, 36.49, 27.61, 26.50. HRMS-EI ( $m/z$ ):  $[\text{M}]^+$  calcd for  $\text{C}_{17}\text{H}_{16}\text{I}_2\text{O}$ , 489.92907; found, 489.92876. Anal. Calcd for  $\text{C}_{17}\text{H}_{16}\text{I}_2\text{O}$ : C, 41.66; H, 3.29. Found: C, 42.20; H, 3.37.

**tert-Butyl-[3-(2,7-diiodo-9-methyl-9H-fluorene-9-yl)propoxy]dimethylsilane (18).** A round-bottom flask was charged with **17** (11.8 g, 24.1 mmol) and DMF (150 mL). *tert*-Butyldimethylchlorosilane (4.67 g, 31 mmol) and imidazole (2.11 g, 31 mmol) were added. The reaction mixture was stirred at room temperature overnight. The reaction mixture was poured into a mixture of  $\text{H}_2\text{O}$  and diethyl ether. The aqueous layer was extracted with diethyl ether. The combined organic layers were dried over anhydrous  $\text{MgSO}_4$ . Volatiles were removed under reduced pressure to give a yellow oil. The product was purified by column chromatography (silica gel, hexanes/dichloromethane = 6:1) to give a white solid (13.68 g, 94%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.71 (d,  $J = 1.4$  Hz, 2H), 7.64 (dd,  $J = 8.0$  Hz, 1.6 Hz, 2H), 7.38 (d,  $J = 8.0$  Hz, 2H), 3.36 (t,  $J = 6.3$  Hz, 2H), 2.02 (m, 2H), 1.43 (s, 3H), 1.39 (s, 1H), 0.88 (s, 9H), 0.83 (m, 2H),  $-0.03$  (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  153.52, 138.80, 136.21, 132.08, 121.66, 93.17, 62.85, 50.85, 36.42, 27.60, 26.63, 25.95, 18.30,  $-5.33$ . HRMS-EI ( $m/z$ ):  $[\text{M}]^+$  calcd for  $\text{C}_{23}\text{H}_{30}\text{I}_2\text{OSi}$ , 604.01555; found, 604.01507. Anal. Calcd for  $\text{C}_{23}\text{H}_{30}\text{I}_2\text{OSi}$ : C, 45.71; H, 5.00. Found: C, 45.94; H, 5.14.

**tert-Butyl-[3-(2,7-diiodo-9-methyl-9H-fluorene-9-yl)propoxy]dimethylsilane (18), Alternative One-Step Procedure.** A mixture of **16** (28.0 g, 65.1 mmol), (3-bromopropoxy)(*tert*-butyl)dimethylsilane (19.1 g, 75.3 mmol), potassium hydroxide (4.42 g, 78.8 mmol), DMSO (150 mL), and 18-crown-6 (1.72 g, 6.5 mmol) was stirred at room temperature overnight. The reaction mixture was extracted with  $\text{Et}_2\text{O}$  (100 mL), and the organic layer was washed with saturated NaCl aqueous solution ( $4 \times 100$  mL) and water ( $3 \times 100$  mL). The organic layer was dried over  $\text{MgSO}_4$ , after which volatiles were removed under reduced pressure. The product was purified by column chromatography (silica gel, hexanes, then hexanes/dichloromethane = 5:1 as eluting solvent), followed by removal of excess (3-bromopropoxy)(*tert*-butyl)dimethylsilane by vacuum distillation (0.04 Torr, 56 °C) to give a pale yellow solid (17.17 g, 44%).

**tert-Butyl-[3-(2,7-biscarbazol-9-yl-9-methyl-9H-fluorene-9-yl)propoxy]dimethylsilane (19).** A mixture **18** (20.7 g, 34.2 mmol), carbazole (11.45 g, 68.5 mmol), copper (8.71 g, 137 mmol),  $\text{K}_2\text{CO}_3$  (37.87 g, 274 mmol), and 18-crown-6 (1.81 g, 6.8 mmol) in 1,2-dichlorobenzene (500 mL) was refluxed at 185 °C under argon for 3 days. The reaction mixture was filtered, and the filtrate was concentrated under reduced pressure. The crude product was purified by two consecutive column chromatographies (silica gel, hexanes/dichloromethane = 3:1 (first), then hexanes/dichloromethane = 1:1 (second)) to give a white solid (20.75 g, 89%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 8.26 (d,  $J = 7.4$  Hz, 4H), 8.03 (d,  $J = 7.7$  Hz, 2H), 7.73 (d,  $J = 1.4$  Hz, 2H), 7.67 (dd,  $J = 8.0$  Hz, 1.9 Hz, 2H), 7.50–7.60 (m, 8H), 7.37–7.43 (m, 4H), 3.54 (t,  $J = 6.6$  Hz, 2H), 2.20 (m, 2H), 1.70 (s, 3H), 1.23 (m, 2H), 0.89 (s, 9H), 0.05 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  153.99, 140.97, 138.63, 136.95, 126.21, 126.00, 123.43, 121.69, 121.23, 120.37, 119.97, 109.78, 63.32, 51.08, 36.93, 28.21, 26.69, 25.91, 18.29,  $-5.33$ . LRMS-EI ( $m/z$ ):  $[\text{M}]^+$  calcd for 682.9; found, 682.4. Anal. Calcd for  $\text{C}_{47}\text{H}_{46}\text{N}_2\text{OSi}$ : C, 82.65; H, 6.79; N, 4.10. Found: C, 82.94; H, 6.91; N, 4.06.

**3-(2,7-Biscarbazol-9-yl-9-methyl-9H-fluorene-9-yl)propan-1-ol (20).** **19** (20.75 g, 30.4 mmol) was dissolved in THF, and tetrabutylammonium fluoride (70 mL of a 1.0 M solution in THF, 70 mmol) was added to the mixture. The resulting mixture was stirred at room temperature, and the reaction progress was monitored by TLC. After the starting material was consumed, the reaction mixture was poured into water and extracted with  $\text{CH}_2\text{Cl}_2$ . The

Table 5. Crystallographic Data for 10, 12, and 13

	10	12	13
formula	C <sub>28</sub> H <sub>33</sub> O <sub>2</sub> NPt	C <sub>30</sub> H <sub>33</sub> O <sub>2</sub> NSPt	C <sub>32</sub> H <sub>35</sub> O <sub>2</sub> NPt
fw	610.64	666.72	660.70
cryst color	yellow	yellow	dark red
cryst habit	prism	plate	Plate
cryst size, mm	0.1 × 0.1 × 0.05	0.2 × 0.1 × 0.02	0.2 × 0.15 × 0.05
cryst syst	monoclinic	monoclinic	triclinic
space group	P2 <sub>1</sub> /c	P2 <sub>1</sub> /n	P1
a, Å	20.193(6)	6.903(2)	10.582(4)
b, Å	5.6385(17)	9.395(3)	10.823(4)
c, Å	21.971(7)	39.788(12)	12.847(5)
α, deg	90	90	97.877(6)
β, deg	100.012(8)	93.562(7)	98.863(6)
γ, deg	90	90	115.270(5)
V, Å <sup>3</sup>	2463.5(13)	2575.5(14)	1280.3(8)
Z	4	4	2
ρ <sub>calc.</sub> , g·cm <sup>-3</sup>	1.646	1.719	1.714
F(000)	1208	1320	656
μ, mm <sup>-1</sup>	5.720	5.557	5.510
T <sub>max</sub> /T <sub>min</sub>	0.751/0.471	0.591/0.895	0.896/0.316
θ range, deg	1.88–26.00	2.05–27.02	2.19 to 26.00
index ranges	–24 ≤ h ≤ 24 –6 ≤ k ≤ 5 –27 ≤ l ≤ 20	–8 ≤ h ≤ 8 –11 ≤ k ≤ 11 –50 ≤ l ≤ 50	–13 ≤ h ≤ 13 –13 ≤ k ≤ 13 –15 ≤ l ≤ 15
no. of rflns collected	12 826	23 085	10 861
no. of indep rflns/R <sub>int</sub>	4762/0.0779	5576/0.0899	4869/0.0477
completeness to θ, %	98.7	99.2	96.9
no. of refined params/restraints	283/20	310/7	313/3
GOF (F <sup>2</sup> )	0.964	1.084	0.973
no. of rflns with I > 2σ(I)	2657	3591	3854
R <sub>1</sub> (F) (I > 2σ(I)) <sup>a</sup>	0.0517	0.0524	0.0370
wR <sub>2</sub> (F <sup>2</sup> ) (all data) <sup>b</sup>	0.1111	0.0847	0.0664
largest diff peak/hole, e·Å <sup>-3</sup>	2.579/–0.777	1.494/–0.857	1.094/–1.232

<sup>a</sup> R<sub>1</sub> = Σ|F<sub>o</sub> – |F<sub>c</sub>||/Σ(F<sub>o</sub>). <sup>b</sup> wR<sub>2</sub> = (Σ[w(F<sub>o</sub><sup>2</sup> – F<sub>c</sub><sup>2</sup>)<sup>2</sup>]/Σ[w(F<sub>o</sub><sup>2</sup>)<sup>2</sup>]<sup>1/2</sup>.

organic layer was dried over anhydrous MgSO<sub>4</sub>. Volatiles were removed under reduced pressure. The crude product was purified by column chromatography (silica gel, hexanes/dichloromethane = 1:1) to give a light yellowish solid (17.28 g, quantitative). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.19 (d, J = 7.7 Hz, 4H), 7.98 (d, J = 7.4 Hz, 2H), 7.65 (d, J = 1.4 Hz, 2H), 7.62 (dd, J = 8.0 Hz, 1.9 Hz, 2H), 7.42–7.53 (m, 8H), 7.30–7.35 (m, 4H), 3.46 (t, J = 6.6 Hz, 2H), 2.14 (m, 2H), 1.63 (s, 3H), 1.14 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>): δ 153.59, 140.78, 138.47, 136.88, 126.12, 125.92, 123.34, 121.52, 121.17, 120.32, 119.94, 109.71, 62.84, 51.06, 36.67, 28.08, 26.76. HRMS-EI (m/z): [M]<sup>+</sup> calcd for C<sub>41</sub>H<sub>32</sub>N<sub>2</sub>O, 568.25146; found, 568.25112. Anal. Calcd for C<sub>41</sub>H<sub>32</sub>N<sub>2</sub>O: C, 86.59; H, 5.67; N, 4.93. Found: C, 86.33; H, 5.65; N, 4.91.

**Toluene-4-sulfonic Acid 3-(2,7-Biscarbazol-9-yl-9-methyl-9H-fluoren-9-yl)propyl Ester (21).** To a solution of **20** (5.0 g, 8.8 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (40 mL) were added *p*-toluenesulfonyl chloride (1.84 g, 9.7 mmol) and pyridine (1.5 mL, 18.5 mmol) at 0 °C. The reaction mixture was gradually warmed to room temperature and stirred at room temperature. The reaction progress was monitored by TLC. After stirring at room temperature for 3 days, the reaction mixture was washed with 1 N HCl. The organic layer was washed with aqueous Na<sub>2</sub>CO<sub>3</sub> solution and water and dried over anhydrous MgSO<sub>4</sub>. Volatiles were removed under reduced pressure. The crude product was purified by column chromatography (silica gel, hexanes/dichloromethane = 1:1) to give a light yellow solid. The solid was triturated and washed with hot MeOH to give a white solid (4.17 g, 66%) after drying under vacuum overnight. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.19 (d, J = 7.7 Hz, 4H), 7.97 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 8.2 Hz, 2H), 7.63 (dd, J = 8.0 Hz, 1.7 Hz, 2H), 7.59 (d, J = 1.6 Hz, 2H), 7.46–7.52 (m, 8H), 7.30–7.38 (m, 4H), 7.16 (d, J = 8.0 Hz, 2H), 3.85 (t, J = 6.3 Hz, 2H), 2.30 (s, 3H), 2.09 (m, 2H), 1.59 (s, 3H), 1.23 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>): δ 152.91, 144.50, 140.71, 138.34, 137.03, 132.81, 129.63, 127.64, 126.29, 126.03, 123.37, 121.34, 121.25, 120.31, 120.02, 109.65, 70.32, 50.77, 36.44,

26.56, 24.57, 21.55. HRMS-EI (m/z): [M]<sup>+</sup> calcd for C<sub>48</sub>H<sub>38</sub>N<sub>2</sub>O<sub>3</sub>S, 722.2603; found, 722.2607. Anal. Calcd for C<sub>48</sub>H<sub>38</sub>N<sub>2</sub>O<sub>3</sub>S: C, 79.75; H, 5.30; N, 3.88; S, 4.44. Found: C, 79.55; H, 5.60; N, 3.90; S, 4.34.

**9-[3-(Bicyclo[2.2.1]hept-5-en-2-ylmethoxy)propyl]-2,7-biscarbazol-9-yl-9-methyl-9H-fluorene (22).** A Schlenk tube was charged with dry THF (25 mL) and excess KH. 5-Norbornene-2-methanol (0.18 g, 1.44 mmol) and **21** (1.2 g, 1.66 mmol) were added to the Schlenk tube sequentially. The resulting mixture was stirred at room temperature for 2 h. The reaction mixture was then quenched with water and extracted with ether. The organic layer was washed with water and dried over anhydrous MgSO<sub>4</sub>. Volatiles were removed under reduced pressure. The crude product was purified by two consecutive column chromatographies (silica gel, hexanes/dichloromethane = 1:1 (first), then hexanes/dichloromethane = 3:1 (second)) to give a colorless glassy solid. The solid was dissolved in THF and precipitated in cold MeOH. The resulting solid was collected by filtration and dried under vacuum to give a white solid (0.57 g, 59%). *Endo* isomer: <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.20 (d, J = 7.7 Hz, 4H), 7.99 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 0.80 Hz, 2H), 7.62 (dd, J = 8.0 Hz, 1.9 Hz, 2H), 7.43–7.54 (m, 8H), 7.30–7.36 (m, 4H), 6.00 (dd, J = 5.8 Hz, 3.0 Hz, 1H), 5.82 (dd, J = 5.8 Hz, 3.0 Hz, 1H), 2.80–3.36 (m, 5H), 2.71 (br, 1H), 2.20–2.30 (m, 1H), 2.10–2.20 (m, 2H), 1.71 (ddd, J = 11.5 Hz, 9.1 Hz, 3.8 Hz, 1H), 1.64 (s, 3H), 1.10–1.38 (m, 4H), 0.38 (ddd, J = 11.5 Hz, 4.4 Hz, 2.5 Hz, 1H). *Endo* and *exo* isomers: <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 153.76, 140.84, 138.54, 136.93, 136.84, 136.40, 136.38, 132.22, 126.10, 125.91, 123.36, 121.60, 121.16, 120.31, 119.91, 109.73, 75.44, 74.51, 70.91, 70.84, 51.17, 49.36, 44.91, 43.96, 43.64, 42.15, 41.50, 38.80, 38.72, 37.05, 29.73, 29.14, 26.74, 25.23. HRMS-EI (m/z): [M]<sup>+</sup> calcd for C<sub>49</sub>H<sub>42</sub>N<sub>2</sub>O, 674.3297; found, 674.3292. Anal. Calcd for C<sub>49</sub>H<sub>42</sub>N<sub>2</sub>O: C, 87.21; H, 6.27; N, 4.15. Found: C, 86.98; H, 6.20; N, 4.08.

**Platinum(II) (1-Phenylisoquinolino-*N,C*<sup>2</sup>)(2,4-pentanedionato-*O,O*) (26).** A mixture of **8** (1.0 g, 1.56 mmol), 2,4-pentanedione (0.344 g, 3.44 mmol), and Na<sub>2</sub>CO<sub>3</sub> (1.65 g, 15.6

mmol) in 2-ethoxyethanol (20 mL) was heated at 100 °C overnight under N<sub>2</sub> atmosphere. The reaction was allowed to cool to room temperature, and H<sub>2</sub>O was added. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with H<sub>2</sub>O and dried over anhydrous MgSO<sub>4</sub>. Volatiles were removed under reduced pressure. The crude product was purified by column chromatography (silica gel, dichloromethane as eluting solvent) to give an orange-brown solid (0.50 g, 64%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.93 (d, *J* = 6.6 Hz, 1H), 8.85 (d, *J* = 8.5 Hz, 1H), 8.07 (dd, *J* = 8.0 Hz, 1.4 Hz, 1H), 7.59–7.82 (m, 4H), 7.40 (d, *J* = 6.3 Hz, 1H), 7.23 (td, *J* = 7.1 Hz, 1.4 Hz, 1H), 7.15 (td, *J* = 7.1 Hz, 1.4 Hz, 1H), 5.47 (s, 1H), 2.010 (s, 3H), 2.005 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>): δ 185.76, 184.00, 168.44, 146.09, 141.43, 139.10, 137.25, 131.01, 130.45, 129.25, 128.41, 128.09, 127.36, 126.10, 125.80, 123.14, 119.44, 102.49, 28.43, 27.26. HRMS-EI (*m/z*): [M]<sup>+</sup> calcd for C<sub>20</sub>H<sub>17</sub>NO<sub>2</sub>Pt, 498.0907; found, 498.0902. Anal. Calcd for C<sub>20</sub>H<sub>17</sub>NO<sub>2</sub>Pt: C, 48.19; H, 3.44; N, 2.81. Found: C, 48.13; H, 3.36; N, 2.71.

**Platinum(II) (2-Phenylbenzothiazolato-*N,C*<sup>2</sup>)(2,4-pentanedionato-*O,O*) (27).** A mixture of **9** (0.5 g, 0.77 mmol), 2,4-pentanedione (0.17 g, 1.7 mmol), and Na<sub>2</sub>CO<sub>3</sub> (0.81 g, 7.67 mmol) in 2-ethoxyethanol (15 mL) was heated at 100 °C for 20 h. The reaction mixture was allowed to cool to room temperature, and H<sub>2</sub>O was added. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with H<sub>2</sub>O and dried over anhydrous MgSO<sub>4</sub>. Volatiles were removed under reduced pressure. The crude product was purified by column chromatography (silica gel, dichloromethane as eluting solvent) to give an orange solid (0.168 g, 43%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 9.17 (d, *J* = 8.5 Hz, 1H), 7.77 (m, 1H), 7.67 (m, 1H), 7.52 (ddd, *J* = 8.5 Hz, 7.1 Hz, 1.4 Hz, 1H), 7.45 (dd, *J* = 7.4 Hz, 1.4 Hz, 1H), 7.39 (ddd, *J* = 8.2 Hz, 7.4 Hz, 1.4 Hz, 1H), 7.18 (td, *J* = 7.4 Hz, 1.4 Hz, 1H), 7.07 (td, *J* = 7.4 Hz, 1.1 Hz, 1H), 5.53 (s, 1H), 2.05 (s, 3H), 2.00 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>): δ 184.97, 183.39, 181.1, 150.68, 140.75, 138.16, 130.63, 130.17, 129.82, 127.35, 125.16, 124.57, 123.61, 121.91, 120.64, 102.05, 28.11, 27.21. HRMS-EI (*m/z*): [M]<sup>+</sup> calcd for C<sub>18</sub>H<sub>15</sub>NO<sub>2</sub>PtS, 504.0471; found, 504.0446. Anal. Calcd for C<sub>18</sub>H<sub>15</sub>NO<sub>2</sub>PtS: C, 42.86; H, 3.00; N, 2.78; S, 6.36. Found: C, 43.12; H, 3.12; N, 2.96; S, 6.42.

**Poly-22.** To a solution of **22** (0.400 g, 0.59 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (10 mL), second-generation Grubbs initiator (10 mg, 0.012 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.5 mL) was added. The reaction mixture was stirred at room temperature and monitored by TLC. After stirring at room temperature for 65 min, the reaction mixture was quenched with few drops of ethyl vinyl ether. The resulting mixture was stirred for additional 30 min. The reaction mixture was poured into MeOH and the resulting solid was collected by filtration, re-dissolved in THF and re-precipitated in MeOH (0.305 g, 76%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.01 (br, 4H), 7.75 (br, 2H), 7.20–7.60 (br, m, 12H), 7.18 (br, 4H), 4.90 (br m, 2H), 0.60–3.20 (br m, 18H). Anal.

(39) SMART and SAINT, Release 5.0, Area Detector Control and Integration Software; Bruker AXS, Analytical X-Ray Instruments: Madison, WI, 1998.

(40) Sheldrick, G. M. SADABS, A Program for Exploiting the Redundancy of Area-detector X-Ray Data; University of Göttingen: Göttingen, Germany, 1999.

(41) Sheldrick, G. M. SHELXTL-97, Program for Solution and Refinement of Crystal Structures; Bruker AXS Inc.: Madison, WI, 1997.

Calcd for (C<sub>49</sub>H<sub>42</sub>N<sub>2</sub>O)<sub>n</sub>: C, 87.21; H, 6.27; N, 4.15. Found: C, 86.63; H, 6.36; N, 4.08.

**Poly-10.** To a solution of **10** (0.19 g, 0.16 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was added second-generation Grubbs initiator (2.8 mg, 0.0033 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL). The reaction mixture was stirred at room temperature and monitored by TLC. After stirring at room temperature for 40 h, the reaction mixture was quenched with few drops of ethyl vinyl ether and stirred for additional 20 min. The reaction mixture was poured into MeOH and the resulting mixture was concentrated under reduced pressure; the resulting solid was collected by vacuum filtration (0.063 g, 63%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.85 (br, 1 H), 7.72 (br, 1H), 7.59 (br, 1H), 7.56 (br, 1H), 7.38 (br, 1H), 7.18 (br, 1H), 7.05 (br, 1H), 5.30 (br m, 2H), 1.13–2.95 (br m, 23H).

**Poly-22-co-10.** To a solution of **22** (0.19 g, 0.148 mmol) and **10** (11.2 mg, 0.018 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (2 mL), second-generation Grubbs initiator (2.8 mg, 0.0033 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) was added. The reaction mixture was stirred at room temperature and monitored by TLC. After stirring at room temperature for 1 h, the reaction mixture was quenched with few drops of ethyl vinyl ether and stirred for additional 20 min. The reaction mixture was poured into MeOH and a white solid was formed. The solid was collected by filtration to give a white solid. The solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and re-precipitated in MeOH (79 mg, 71%). This polymer was also obtained (58 mg, 52%) in an analogous method using the third-generation Grubbs initiator (3 mg, 0.0033 mmol). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.84 (br, ca. 0.15H), 8.01 (br, 4H), 7.75 (br, 2H), 7.20–7.60 (br, m, 12H), 7.18 (br, 4H), 6.80–7.10 (br m, ca. 0.45H), 4.90 (br m, 2H), 0.60–3.20 (br m, 18H).

**Poly-22-co-11.** This polymer was obtained (44 mg, 40%) in the same way as poly-22-co-10 using second-generation Grubbs initiator and using **11** (11.1 mg) in place of **10**. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.82 (br, ca. 0.15H), 8.01 (br, 4H), 7.75 (br, 2H), 7.20–7.60 (br, m, 12H), 7.18 (br, 4H), 6.90 (br, 0.3H), 6.47 (br, 0.3H), 4.90 (br m, 2H), 0.60–3.20 (br m, 18H).

**Poly-22-co-12.** This polymer was obtained (89.3 mg, 79%) in the same way as poly-22-co-11 using **12** (11.1 mg) in place of **11**. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.76 (br, ca. 0.15H), 8.01 (br, 4H), 7.75 (br, 2H), 7.20–7.60 (br, m, 12H), 7.18 (br, 4H), 6.70 (br, ca. 0.15H), 4.90 (br m, 2H), 0.60–3.20 (br m, 18H).

**X-ray Diffraction.** X-ray experiments were carried out using a SMART 1000 CCD diffractometer ( $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$ , graphite monochromator,  $\omega$ -scans) at 120 K. The details of data collection and crystal structure refinement, for which we used SAINT Plus,<sup>39</sup> SADABS,<sup>40</sup> and SHELXTL-97<sup>41</sup> program packages, are summarized in Table 5.

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**Supporting Information Available:** Figures showing NMR characterization of **4** and polymers and showing disorder models used for crystals of **10**, **12**, and **13** (PDF format). Crystallographic data for **10**, **12**, and **13** (CIF format). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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