

**SUPPLEMENTARY INFORMATION**

**Multifunctional Pt(II) metallomesogens exhibiting luminescence and proton conductivity in the mesophase near room-temperature**

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## Structural characterization of Pt(II) compounds

### Compounds [PtCl<sub>2</sub>(Hpz<sup>R(n,n)py</sup>)] 1-8

[PtCl<sub>2</sub>(Hpz<sup>R(4,4)py</sup>)] (**1**): yellow solid (48%). Found: C, 40.7; H, 4.4; N, 6.5. PtC<sub>22</sub>H<sub>27</sub>N<sub>3</sub>O<sub>2</sub>Cl<sub>2</sub>·H<sub>2</sub>O requires C, 40.7; H, 4.5; N, 6.5%.  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3304w  $\nu(\text{N}-\text{H})$ , 2918 – 2850m  $\nu(\text{C}-\text{H})_{\text{aliph}}$ , 1597s  $\nu(\text{C}=\text{C} + \text{C}=\text{N})$ , 765s  $\gamma(\text{C}-\text{H})_{\text{py}}$ .  $\delta_{\text{H}}$  (300.16 MHz; CDCl<sub>3</sub>; TMS): 1.00 (6H, t, <sup>3</sup>J 7.3, CH<sub>3</sub>), 1.52 (4H, m, CH<sub>2</sub>), 1.78 (4H, qt, <sup>3</sup>J 6.7, CH<sub>2</sub>), 3.99 (4H, t, <sup>3</sup>J 6.5, OCH<sub>2</sub>), 6.55 (1H, t, <sup>4</sup>J 2.1, Hp), 6.68 (2H, d, <sup>4</sup>J 2.1, Ho), 7.06 (1H, d, <sup>4</sup>J 1.7, H4'), 7.44 (1H, ddd, <sup>3</sup>J 7.4, 5.8, <sup>4</sup>J 1.2, H5), 7.84 (1H, d, <sup>3</sup>J 7.5, H3), 8.11 (1H, ddd, <sup>3</sup>J 7.7, 7.7, <sup>4</sup>J 1.3, H4), 9.43 (1H, d, <sup>3</sup>J 5.8, H6), 11.44 (1H, br, NH).

[PtCl<sub>2</sub>(Hpz<sup>R(6,6)py</sup>)] (**2**): yellow solid (45%). Found: C, 44.7; H, 5.0; N, 6.5. PtC<sub>26</sub>H<sub>35</sub>N<sub>3</sub>O<sub>2</sub>Cl<sub>2</sub>·0.4H<sub>2</sub>O requires C, 44.9; H, 5.2; N, 6.1%.  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3377w  $\nu(\text{N}-\text{H})$ , 2928 – 2859m  $\nu(\text{C}-\text{H})_{\text{aliph}}$ , 1596s  $\nu(\text{C}=\text{C} + \text{C}=\text{N})$ , 769s  $\gamma(\text{C}-\text{H})_{\text{py}}$ .  $\delta_{\text{H}}$  (300.16 MHz; CDCl<sub>3</sub>; TMS): 0.92 (6H, t, <sup>3</sup>J 6.8, CH<sub>3</sub>), 1.35 (12H, m, CH<sub>2</sub>), 1.80 (4H, qt, <sup>3</sup>J 6.6, CH<sub>2</sub>), 3.98 (4H, t, <sup>3</sup>J 6.5, OCH<sub>2</sub>), 6.54 (1H, t, <sup>4</sup>J 2.0, Hp), 6.67 (2H, d, <sup>4</sup>J 2.0, Ho), 7.07 (1H, s, H4'), 7.42 (1H, pt, <sup>3</sup>J 6.5, H5), 7.85 (1H, d, <sup>3</sup>J 7.7, H3), 8.11 (1H, pt, <sup>3</sup>J 7.6, H4), 9.38 (1H, d, <sup>3</sup>J 5.8, H6), 11.48 (1H, s, NH).

[PtCl<sub>2</sub>(Hpz<sup>R(8,8)py</sup>)] (**3**): yellow solid (49%). Found: C, 47.5; H, 5.8; N, 6.0. PtC<sub>30</sub>H<sub>43</sub>N<sub>3</sub>O<sub>2</sub>Cl<sub>2</sub>·0.5H<sub>2</sub>O requires C, 47.9; H, 5.9; N, 5.6%.  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3363w  $\nu(\text{N}-\text{H})$ , 2927 – 2856m  $\nu(\text{C}-\text{H})_{\text{aliph}}$ , 1596s  $\nu(\text{C}=\text{C} + \text{C}=\text{N})$ , 770s  $\gamma(\text{C}-\text{H})_{\text{py}}$ .  $\delta_{\text{H}}$  (300.16 MHz; CDCl<sub>3</sub>; TMS): 0.89 (6H, t, <sup>3</sup>J 6.9, CH<sub>3</sub>), 1.30 (20H, m, CH<sub>2</sub>), 1.80 (4H, qt, <sup>3</sup>J 6.6, CH<sub>2</sub>), 3.97 (4H, t, <sup>3</sup>J 6.5, OCH<sub>2</sub>), 6.52 (1H, t, <sup>4</sup>J 1.9, Hp), 6.67 (2H, d, <sup>4</sup>J 2.0, Ho), 7.08 (1H, s, H4'), 7.41 (1H, ddd, <sup>3</sup>J 7.4, 5.8, <sup>4</sup>J 1.0, H5), 7.86 (1H, d, <sup>3</sup>J 7.7, H3), 8.11 (1H, ddd, <sup>3</sup>J 7.7, 7.7, <sup>4</sup>J 1.1, H4), 9.35 (1H, d, <sup>3</sup>J 5.8, H6), 11.49 (1H, s, NH).

[PtCl<sub>2</sub>(Hpz<sup>R(10,10)py</sup>)] (**4**): yellow solid (45%). Found: C, 50.5; H, 6.4; N, 5.5. PtC<sub>34</sub>H<sub>51</sub>N<sub>3</sub>O<sub>2</sub>Cl<sub>2</sub>·0.5H<sub>2</sub>O requires C, 50.5; H, 6.5; N, 5.2%.  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3389w  $\nu(\text{N}-\text{H})$ , 2922 – 2852m  $\nu(\text{C}-\text{H})_{\text{aliph}}$ , 1601s  $\nu(\text{C}=\text{C} + \text{C}=\text{N})$ , 773s  $\gamma(\text{C}-\text{H})_{\text{py}}$ .  $\delta_{\text{H}}$  (300.16 MHz; CDCl<sub>3</sub>; TMS): 0.88 (6H, t, <sup>3</sup>J 6.9, CH<sub>3</sub>), 1.28 (28H, m, CH<sub>2</sub>), 1.81 (4H, qt, <sup>3</sup>J 6.7, CH<sub>2</sub>), 3.98 (4H, t, <sup>3</sup>J 6.4, OCH<sub>2</sub>), 6.55 (1H, t, <sup>4</sup>J 1.9, Hp), 6.68 (2H, d, <sup>4</sup>J 2.0, Ho), 7.04 (1H, s, H4'), 7.41 (1H, ddd, <sup>3</sup>J 7.7, 5.8, <sup>4</sup>J 1.0, H5), 7.81 (1H, d, <sup>3</sup>J 7.5, H3), 8.11 (1H, ddd, <sup>3</sup>J 7.7, 7.7, <sup>4</sup>J 1.1, H4), 9.44 (1H, d, <sup>3</sup>J 5.7, H6), 11.43 (1H, s, NH).

[PtCl<sub>2</sub>(Hpz<sup>R(12,12)py</sup>)] (**5**): yellow solid (53%). Found: C, 52.3; H, 6.8; N, 5.0. PtC<sub>38</sub>H<sub>59</sub>N<sub>3</sub>O<sub>2</sub>Cl<sub>2</sub>·H<sub>2</sub>O requires C, 52.2; H, 7.0; N, 4.8%.  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3381w  $\nu(\text{N}-\text{H})$ , 2926 – 2856m  $\nu(\text{C}-\text{H})_{\text{aliph}}$ , 1596s  $\nu(\text{C}=\text{C} + \text{C}=\text{N})$ , 770m  $\gamma(\text{C}-\text{H})_{\text{py}}$ .  $\delta_{\text{H}}$  (300.16 MHz; CDCl<sub>3</sub>; TMS): 0.88 (6H, t, <sup>3</sup>J 6.9, CH<sub>3</sub>), 1.26 (36H, m, CH<sub>2</sub>), 1.80 (4H, qt, <sup>3</sup>J 6.6, CH<sub>2</sub>), 3.97 (4H, t, <sup>3</sup>J 6.5, OCH<sub>2</sub>), 6.52 (1H, t, <sup>4</sup>J 2.0, Hp), 6.66 (2H, d, <sup>4</sup>J 2.0, Ho), 7.09 (1H, d, <sup>4</sup>J 1.1, H4'), 7.40 (1H, ddd, <sup>3</sup>J 7.4, 5.8, <sup>4</sup>J 1.2, H5), 7.87 (1H, d, <sup>3</sup>J 7.6, H3), 8.10 (1H, ddd, <sup>3</sup>J 7.7, 7.7, <sup>4</sup>J 1.2, H4), 9.34 (1H, d, <sup>3</sup>J 5.8, H6), 11.47 (1H, br, NH).  $\delta_{\text{C}}$  (75.48 MHz; CDCl<sub>3</sub>; TMS): 14.1 (CH<sub>3</sub>), 22.7 – 31.9 (CH<sub>2</sub>), 68.5 (OCH<sub>2</sub>), 102.4 (C4'), 103.4 (Cp), 104.1 (Co), 122.6 (C3), 125.0 (C5), 127.6 (Ci), 139.8 (C4), 144.9 (C3'), 149.3 (C6), 151.2 (C2), 152.1 (C5'), 161.0 (Cm).

**[PtCl<sub>2</sub>(Hpz<sup>R(14,14)py]) (6)</sup>**: yellow solid (50%). Found: C, 55.5; H, 7.4; N, 4.7. PtC<sub>42</sub>H<sub>67</sub>N<sub>3</sub>O<sub>2</sub>Cl<sub>2</sub> requires C, 55.3; H, 7.4; N, 4.6%.  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3202w  $\nu(\text{N}-\text{H})$ , 2919 – 2850s  $\nu(\text{C}-\text{H})_{\text{aliph}}$ , 1598m  $\nu(\text{C}=\text{C} + \text{C}=\text{N})$ , 775w  $\gamma(\text{C}-\text{H})_{\text{py}}$ .  $\delta_{\text{H}}$  (300.16 MHz; CDCl<sub>3</sub>; TMS): 0.87 (6H, t, <sup>3</sup>J 6.9, CH<sub>3</sub>), 1.26 (44H, m, CH<sub>2</sub>), 1.80 (4H, qt, <sup>3</sup>J 6.7, CH<sub>2</sub>), 3.98 (4H, t, <sup>3</sup>J 6.5, OCH<sub>2</sub>), 6.54 (1H, t, <sup>4</sup>J 2.0, Hp), 6.68 (2H, d, <sup>4</sup>J 2.0, Ho), 7.05 (1H, s, H4'), 7.44 (1H, ddd, <sup>3</sup>J 7.4, 5.8, <sup>4</sup>J 1.0, H5), 7.83 (1H, d, <sup>3</sup>J 7.6, H3), 8.12 (1H, ddd, <sup>3</sup>J 7.7, 7.7, <sup>4</sup>J 1.1, H4), 9.44 (1H, d, <sup>3</sup>J 5.8, H6), 11.54 (1H, s, NH).

**[PtCl<sub>2</sub>(Hpz<sup>R(16,16)py]) (7)</sup>**: yellow solid (37%). Found: C, 57.6; H, 7.7; N, 4.4. PtC<sub>46</sub>H<sub>75</sub>N<sub>3</sub>O<sub>2</sub>Cl<sub>2</sub> requires C, 57.1; H, 7.8; N, 4.3%.  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3200w  $\nu(\text{N}-\text{H})$ , 2919 – 2850s  $\nu(\text{C}-\text{H})_{\text{aliph}}$ , 1597m  $\nu(\text{C}=\text{C} + \text{C}=\text{N})$ , 776w  $\gamma(\text{C}-\text{H})_{\text{py}}$ .  $\delta_{\text{H}}$  (300.16 MHz; CDCl<sub>3</sub>; TMS): 0.87 (6H, t, <sup>3</sup>J 6.9, CH<sub>3</sub>), 1.25 (52H, m, CH<sub>2</sub>), 1.80 (4H, qt, <sup>3</sup>J 6.8, CH<sub>2</sub>), 3.98 (4H, t, <sup>3</sup>J 6.5, OCH<sub>2</sub>), 6.55 (1H, t, <sup>4</sup>J 2.0, Hp), 6.68 (2H, d, <sup>4</sup>J 2.1, Ho), 7.03 (1H, d, <sup>4</sup>J 1.1, H4'), 7.46 (1H, ddd, <sup>3</sup>J 7.5, 5.8, <sup>4</sup>J 1.3, H5), 7.80 (1H, d, <sup>3</sup>J 7.5, H3), 8.12 (1H, ddd, <sup>3</sup>J 7.8, 7.8, <sup>4</sup>J 1.4, H4), 9.49 (1H, d, <sup>3</sup>J 5.8, H6), 11.54 (1H, br, NH).

**[PtCl<sub>2</sub>(Hpz<sup>R(18,18)py]) (8)</sup>**: yellow solid (40%). Found: C, 59.2; H, 8.2; N, 4.0. PtC<sub>50</sub>H<sub>83</sub>N<sub>3</sub>O<sub>2</sub>Cl<sub>2</sub> requires C, 58.6; H, 8.2; N, 4.1%.  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3199w  $\nu(\text{N}-\text{H})$ , 2920 – 2850s  $\nu(\text{C}-\text{H})_{\text{aliph}}$ , 1598m  $\nu(\text{C}=\text{C} + \text{C}=\text{N})$ , 773w  $\gamma(\text{C}-\text{H})_{\text{py}}$ .  $\delta_{\text{H}}$  (300.16 MHz; CDCl<sub>3</sub>; TMS): 0.88 (6H, t, <sup>3</sup>J 6.9, CH<sub>3</sub>), 1.25 (60H, m, CH<sub>2</sub>), 1.80 (4H, qt, <sup>3</sup>J 6.9, CH<sub>2</sub>), 3.99 (4H, t, <sup>3</sup>J 6.5, OCH<sub>2</sub>), 6.55 (1H, t, <sup>4</sup>J 2.0, Hp), 6.68 (2H, d, <sup>4</sup>J 2.0, Ho), 7.05 (1H, s, H4'), 7.45 (1H, ddd, <sup>3</sup>J 7.5, 5.8, <sup>4</sup>J 1.2, H5), 7.80 (1H, d, <sup>3</sup>J 7.5, H3), 8.11 (1H, ddd, <sup>3</sup>J 7.7, 7.7, <sup>4</sup>J 1.2, H4), 9.49 (1H, d, <sup>3</sup>J 5.8, H6), 11.53 (1H, s, NH).

### Compounds [PtCl<sub>2</sub>(Hpz<sup>R(n,n)iq</sup>)] 9-16

**[PtCl<sub>2</sub>(Hpz<sup>R(4,4)iq]) (9)</sup>**: yellow solid (47%). Found: C, 44.9; H, 4.4; N, 6.3. PtC<sub>26</sub>H<sub>29</sub>N<sub>3</sub>O<sub>2</sub>Cl<sub>2</sub>·H<sub>2</sub>O requires C, 44.6; H, 4.5; N, 6.0%.  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3373w  $\nu(\text{N}-\text{H})$ , 2919 – 2851m  $\nu(\text{C}-\text{H})_{\text{aliph}}$ , 1637 – 1595s  $\nu(\text{C}=\text{C} + \text{C}=\text{N})$ , 752 – 718m  $\gamma(\text{C}-\text{H})_{\text{iq}}$ .  $\delta_{\text{H}}$  (300.16 MHz; CDCl<sub>3</sub>; TMS): 1.02 (6H, t, <sup>3</sup>J 7.4, CH<sub>3</sub>), 1.55 (4H, sx, <sup>3</sup>J 7.2, CH<sub>2</sub>), 1.81 (4H, qt, <sup>3</sup>J 6.7, CH<sub>2</sub>), 4.01 (4H, t, <sup>3</sup>J 6.5, OCH<sub>2</sub>), 6.54 (1H, t, <sup>4</sup>J 1.9, Hp), 6.61 (2H, d, <sup>4</sup>J 1.9, Ho), 7.21 (1H, br, H4'), 7.69 (2H, m, H7, H8), 7.96 (1H, pt, <sup>3</sup>J 6.5, H6), 8.05 (1H, d, <sup>3</sup>J 8.5, H5), 8.31 (1H, s, H4), 9.71 (1H, s, H1), 10.91 (1H, s, NH).

**[PtCl<sub>2</sub>(Hpz<sup>R(6,6)iq]) (10)</sup>**: yellow solid (54%). Found: C, 48.5; H, 5.0; N, 5.9. PtC<sub>30</sub>H<sub>37</sub>N<sub>3</sub>O<sub>2</sub>Cl<sub>2</sub> requires C, 48.8; H, 5.1; N, 5.7%.  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3377w  $\nu(\text{N}-\text{H})$ , 2929 – 2869m  $\nu(\text{C}-\text{H})_{\text{aliph}}$ , 1636 – 1594s  $\nu(\text{C}=\text{C} + \text{C}=\text{N})$ , 753 – 717m  $\gamma(\text{C}-\text{H})_{\text{iq}}$ .  $\delta_{\text{H}}$  (300.16 MHz; CDCl<sub>3</sub>; TMS): 0.93 (6H, t, <sup>3</sup>J 6.9, CH<sub>3</sub>), 1.38 (12H, m, CH<sub>2</sub>), 1.82 (4H, qt, <sup>3</sup>J 6.5, CH<sub>2</sub>), 4.00 (4H, t, <sup>3</sup>J 6.5, OCH<sub>2</sub>), 6.54 (1H, t, <sup>4</sup>J 2.1, Hp), 6.65 (2H, d, <sup>4</sup>J 2.1, Ho), 7.16 (1H, d, <sup>4</sup>J 1.7, H4'), 7.70 (1H, ddd, <sup>3</sup>J 8.1, 6.8, <sup>4</sup>J 1.3, H7), 7.84 (1H, d, <sup>3</sup>J 8.0, H8), 7.97 (1H, ddd, <sup>3</sup>J 7.9, 6.8, <sup>4</sup>J 1.1, H6), 8.03 (1H, d, <sup>3</sup>J 8.1, H5), 8.26 (1H, s, H4), 9.84 (1H, s, H1), 11.17 (1H, br, NH).

**[PtCl<sub>2</sub>(Hpz<sup>R(8,8)iq]) (11)</sup>**: yellow solid (43%). Found: C, 51.2; H, 5.6; N, 5.5. PtC<sub>34</sub>H<sub>45</sub>N<sub>3</sub>O<sub>2</sub>Cl<sub>2</sub> requires C, 51.4; H, 5.7; N, 5.3%.  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3370w  $\nu(\text{N}-\text{H})$ , 2924 – 2854s  $\nu(\text{C}-\text{H})_{\text{aliph}}$ , 1638 – 1595s  $\nu(\text{C}=\text{C} + \text{C}=\text{N})$ , 753 – 718m  $\gamma(\text{C}-\text{H})_{\text{iq}}$ .  $\delta_{\text{H}}$  (300.16 MHz; CDCl<sub>3</sub>; TMS): 0.91 (6H, t, <sup>3</sup>J 6.8, CH<sub>3</sub>), 1.32 (20H, m, CH<sub>2</sub>),

1.82 (4H, qt,  $^3J$  6.8, CH<sub>2</sub>), 3.99 (4H, t,  $^3J$  6.5, OCH<sub>2</sub>), 6.51 (1H, t,  $^4J$  1.9, Hp), 6.57 (2H, d,  $^4J$  1.9, Ho), 7.24 (1H, br, H4'), 7.60 (2H, m, H7, H8), 7.95 (1H, ddd,  $^3J$  8.0, 6.4,  $^4J$  1.3, H6), 8.06 (1H, d,  $^3J$  8.2, H5), 8.34 (1H, s, H4), 9.56 (1H, s, H1), 10.82 (1H, s, NH).

**[PtCl<sub>2</sub>(Hpz<sup>R(10,10)iq</sup>)]** (**12**): yellow solid (46%). Found: C, 53.7; H, 6.2; N, 5.2. PtC<sub>38</sub>H<sub>53</sub>N<sub>3</sub>O<sub>2</sub>Cl<sub>2</sub> requires C, 53.7; H, 6.3; N, 4.9%.  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3377w  $\nu(\text{N}-\text{H})$ , 2923 – 2853s  $\nu(\text{C}-\text{H})_{\text{aliph}}$ , 1638 – 1596s  $\nu(\text{C}=\text{C} + \text{C}=\text{N})$ , 752 – 718m  $\gamma(\text{C}-\text{H})_{\text{iq}}$ .  $\delta_{\text{H}}$  (300.16 MHz; CDCl<sub>3</sub>; TMS): 0.89 (6H, t,  $^3J$  6.9, CH<sub>3</sub>), 1.29 (28H, m, CH<sub>2</sub>), 1.82 (4H, qt,  $^3J$  6.8, CH<sub>2</sub>), 3.99 (4H, t,  $^3J$  6.5, OCH<sub>2</sub>), 6.51 (1H, t,  $^4J$  2.0, Hp), 6.58 (2H, d,  $^4J$  2.0, Ho), 7.23 (1H, br, H4'), 7.62 (2H, m, H7, H8), 7.95 (1H, ddd,  $^3J$  8.0, 5.8,  $^4J$  2.1, H6), 8.05 (1H, d,  $^3J$  8.3, H5), 8.34 (1H, s, H4), 9.59 (1H, s, H1), 10.85 (1H, s, NH).

**[PtCl<sub>2</sub>(Hpz<sup>R(12,12)iq</sup>)]** (**13**): yellow solid (53%). Found: C, 55.7; H, 6.6; N, 4.9. PtC<sub>42</sub>H<sub>61</sub>N<sub>3</sub>O<sub>2</sub>Cl<sub>2</sub> requires C, 55.7; H, 6.8; N, 4.6%.  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3242w  $\nu(\text{N}-\text{H})$ , 2920 – 2851s  $\nu(\text{C}-\text{H})_{\text{aliph}}$ , 1639 – 1595s  $\nu(\text{C}=\text{C} + \text{C}=\text{N})$ , 754 – 718m  $\gamma(\text{C}-\text{H})_{\text{iq}}$ .  $\delta_{\text{H}}$  (300.16 MHz; CDCl<sub>3</sub>; TMS): 0.88 (6H, t,  $^3J$  6.9, CH<sub>3</sub>), 1.28 (36H, m, CH<sub>2</sub>), 1.82 (4H, qt,  $^3J$  6.7, CH<sub>2</sub>), 3.99 (4H, t,  $^3J$  6.5, OCH<sub>2</sub>), 6.52 (1H, t,  $^4J$  1.9, Hp), 6.62 (2H, d,  $^4J$  1.9, Ho), 7.20 (1H, d,  $^4J$  1.0, H4'), 7.69 (2H, m, H7, H8), 7.96 (1H, ddd,  $^3J$  7.8, 6.5,  $^4J$  1.7, H6), 8.04 (1H, d,  $^3J$  7.9, H5), 8.30 (1H, s, H4), 9.72 (1H, s, H1), 11.11 (1H, br, NH).  $\delta_{\text{C}}$  (75.48 MHz; CDCl<sub>3</sub>; TMS): 14.1 (CH<sub>3</sub>), 22.7 – 31.9 (CH<sub>2</sub>), 68.5 (OCH<sub>2</sub>), 101.5 (C4'), 103.3 (Co), 103.9 (Cp), 120.6 (C4), 127.0 (Ci), 127.3 (C10), 127.8 (C5), 128.7 (C8), 129.8 (C7), 133.9 (C6), 134.7 (C9), 143.0 (C3), 144.1 (C3'), 151.8 (C5'), 152.6 (C1), 161.0 (Cm).

**[PtCl<sub>2</sub>(Hpz<sup>R(14,14)iq</sup>)]** (**14**): yellow solid (54%). Found: C, 57.6; H, 7.1; N, 4.7. PtC<sub>46</sub>H<sub>69</sub>N<sub>3</sub>O<sub>2</sub>Cl<sub>2</sub> requires C, 57.4; H, 7.2; N, 4.4%.  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3247w  $\nu(\text{N}-\text{H})$ , 2920 – 2851s  $\nu(\text{C}-\text{H})_{\text{aliph}}$ , 1639 – 1596m  $\nu(\text{C}=\text{C} + \text{C}=\text{N})$ , 753 – 719m  $\gamma(\text{C}-\text{H})_{\text{iq}}$ .  $\delta_{\text{H}}$  (300.16 MHz; CDCl<sub>3</sub>; TMS): 0.88 (6H, t,  $^3J$  6.9, CH<sub>3</sub>), 1.27 (44H, m, CH<sub>2</sub>), 1.82 (4H, qt,  $^3J$  6.5, CH<sub>2</sub>), 3.99 (4H, t,  $^3J$  6.5, OCH<sub>2</sub>), 6.52 (1H, t,  $^4J$  1.9, Hp), 6.59 (2H, d,  $^4J$  2.0, Ho), 7.22 (1H, br, H4'), 7.65 (2H, m, H7, H8), 7.95 (1H, ddd,  $^3J$  8.1, 6.7,  $^4J$  1.5, H6), 8.05 (1H, d,  $^3J$  8.2, H5), 8.33 (1H, s, H4), 9.64 (1H, s, H1), 10.84 (1H, s, NH).

**[PtCl<sub>2</sub>(Hpz<sup>R(16,16)iq</sup>)]** (**15**): yellow solid (41%). Found: C, 59.0; H, 7.6; N, 4.1. PtC<sub>50</sub>H<sub>77</sub>N<sub>3</sub>O<sub>2</sub>Cl<sub>2</sub> requires C, 59.0; H, 7.6; N, 4.1%.  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3250w  $\nu(\text{N}-\text{H})$ , 2919 – 2851s  $\nu(\text{C}-\text{H})_{\text{aliph}}$ , 1639 – 1597m  $\nu(\text{C}=\text{C} + \text{C}=\text{N})$ , 751 – 719m  $\gamma(\text{C}-\text{H})_{\text{iq}}$ .  $\delta_{\text{H}}$  (300.16 MHz; CDCl<sub>3</sub>; TMS): 0.87 (6H, t,  $^3J$  6.9, CH<sub>3</sub>), 1.26 (52H, m, CH<sub>2</sub>), 1.81 (4H, qt,  $^3J$  6.5, CH<sub>2</sub>), 3.99 (4H, t,  $^3J$  6.5, OCH<sub>2</sub>), 6.53 (1H, t,  $^4J$  1.9, Hp), 6.63 (2H, d,  $^4J$  2.0, Ho), 7.17 (1H, s, H4'), 7.69 (1H, ddd,  $^3J$  7.9, 6.8,  $^4J$  1.0, H7), 7.80 (1H, d,  $^3J$  8.3, H8), 7.96 (1H, pt,  $^3J$  6.7, H6), 8.03 (1H, d,  $^3J$  8.2, H5), 8.27 (1H, s, H4), 9.80 (1H, s, H1), 11.08 (1H, s, NH).

**[PtCl<sub>2</sub>(Hpz<sup>R(18,18)iq</sup>)]** (**16**): yellow solid (46%). Found: C, 60.9; H, 7.7; N, 4.1. PtC<sub>54</sub>H<sub>85</sub>N<sub>3</sub>O<sub>2</sub>Cl<sub>2</sub> requires C, 60.4; H, 8.0; N, 3.9%.  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3241w  $\nu(\text{N}-\text{H})$ , 2919 – 2850s  $\nu(\text{C}-\text{H})_{\text{aliph}}$ , 1639 – 1597m  $\nu(\text{C}=\text{C} + \text{C}=\text{N})$ , 751 – 719m  $\gamma(\text{C}-\text{H})_{\text{iq}}$ .  $\delta_{\text{H}}$  (300.16 MHz; CDCl<sub>3</sub>; TMS): 0.87 (6H, t,  $^3J$  6.8, CH<sub>3</sub>), 1.25 (60H, m, CH<sub>2</sub>), 1.81 (4H, qt,  $^3J$  6.4, CH<sub>2</sub>), 3.99 (4H, t,  $^3J$  6.4, OCH<sub>2</sub>), 6.52 (1H, t,  $^4J$  2.1, Hp), 6.61 (2H, d,  $^4J$  2.1,

Ho), 7.19 (1H, s, H4'), 7.69 (2H, m, H7, H8), 7.95 (1H, pt,  $^3J$  6.7, H6), 8.03 (1H, d,  $^3J$  8.3, H5), 8.29 (1H, s, H4), 9.72 (1H, s, H1), 11.00 (1H, s, NH).

### Compounds [Pt(pz<sup>R(12,12)py</sup>)(pz<sup>R(n,n)py</sup>)] 17-23

[Pt(pz<sup>R(12,12)py</sup>)(pz<sup>R(4,4)py</sup>)] (17): red solid (36%). Found: C, 61.1; H, 7.1; N, 6.9. PtC<sub>60</sub>H<sub>84</sub>N<sub>6</sub>O<sub>4</sub>·0.3CHCl<sub>3</sub> requires C, 61.2; H, 7.2; N, 7.1%.  $\nu_{max}/\text{cm}^{-1}$ : 2925 – 2854s  $\nu(\text{C–H})_{\text{aliph}}$ , 1599s  $\nu(\text{C=C + C=N})$ , 757m  $\gamma(\text{C–H})_{\text{py}}$ .  $\delta_{\text{H}}$  (300.16 MHz; CDCl<sub>3</sub>; TMS): 0.88 (6H, t,  $^3J$  6.9, CH<sub>3</sub>), 1.02 (6H, t,  $^3J$  7.3, CH<sub>3</sub>), 1.27 (40H, m, CH<sub>2</sub>), 1.84 (8H, qt,  $^3J$  6.4, CH<sub>2</sub>), 4.04 (4H, t,  $^3J$  6.5, OCH<sub>2</sub>), 4.06 (4H, t,  $^3J$  6.5, OCH<sub>2</sub>), 6.43 (2H, m, Hp), 6.83 (1H, s, H4'), 6.84 (1H, s, H4'), 7.05 (4H, m, Ho), 7.21 (2H, ddd,  $^3J$  7.1, 5.8,  $^4J$  1.1, H5), 7.56 (2H, d,  $^3J$  7.8, H3), 7.84 (2H, pt,  $^3J$  7.8, H4), 10.73 (2H, d,  $^3J$  5.5, H6).

[Pt(pz<sup>R(12,12)py</sup>)(pz<sup>R(6,6)py</sup>)] (18): red solid (37%). Found: C, 63.0; H, 7.5; N, 7.0. PtC<sub>64</sub>H<sub>92</sub>N<sub>6</sub>O<sub>4</sub>·0.1CHCl<sub>3</sub> requires C, 63.3; H, 7.6; N, 6.9%.  $\nu_{max}/\text{cm}^{-1}$ : 2925 – 2854s  $\nu(\text{C–H})_{\text{aliph}}$ , 1600s  $\nu(\text{C=C + C=N})$ , 757m  $\gamma(\text{C–H})_{\text{py}}$ .  $\delta_{\text{H}}$  (300.16 MHz; CDCl<sub>3</sub>; TMS): 0.88 (6H, t,  $^3J$  6.9, CH<sub>3</sub>), 0.93 (6H, t,  $^3J$  6.9, CH<sub>3</sub>), 1.27 (48H, m, CH<sub>2</sub>), 1.85 (8H, qt,  $^3J$  6.4, CH<sub>2</sub>), 4.06 (8H, t,  $^3J$  6.5, OCH<sub>2</sub>), 6.44 (2H, t,  $^4J$  2.0, Hp), 6.86 (1H, s, H4'), 7.08 (1H, s, H4'), 7.05 (4H, d,  $^4J$  2.1, Ho), 7.21 (2H, pt,  $^3J$  7.2, H5), 7.55 (2H, d,  $^3J$  6.7, H3), 7.84 (2H, pt,  $^3J$  7.7, H4), 10.76 (2H, d,  $^3J$  6.0, H6).

[Pt(pz<sup>R(12,12)py</sup>)(pz<sup>R(8,8)py</sup>)] (19): red solid (34%). Found: C, 62.7; H, 7.5; N, 6.5. PtC<sub>68</sub>H<sub>100</sub>N<sub>6</sub>O<sub>4</sub>·0.4CHCl<sub>3</sub> requires C, 62.8; H, 7.7; N, 6.4%.  $\nu_{max}/\text{cm}^{-1}$ : 2925 – 2854s  $\nu(\text{C–H})_{\text{aliph}}$ , 1599s  $\nu(\text{C=C + C=N})$ , 759m  $\gamma(\text{C–H})_{\text{py}}$ .  $\delta_{\text{H}}$  (300.16 MHz; CDCl<sub>3</sub>; TMS): 0.88 (6H, t,  $^3J$  6.8, CH<sub>3</sub>), 0.90 (6H, t,  $^3J$  6.5, CH<sub>3</sub>), 1.27 (56H, m, CH<sub>2</sub>), 1.85 (8H, qt,  $^3J$  6.4, CH<sub>2</sub>), 4.06 (8H, t,  $^3J$  6.6, OCH<sub>2</sub>), 6.43 (2H, t,  $^4J$  1.9, Hp), 6.82 (2H, s, H4'), 7.06 (4H, d,  $^4J$  2.0, Ho), 7.17 (2H, pt,  $^3J$  6.4, H5), 7.49 (2H, d,  $^3J$  7.5, H3), 7.76 (2H, pt,  $^3J$  7.3, H4), 10.73 (2H, d,  $^3J$  5.5, H6).  $\delta_{\text{C}}$  (75.48 MHz; CDCl<sub>3</sub>; TMS): 14.1 (CH<sub>3</sub>), 22.7 – 31.9 (CH<sub>2</sub>), 68.0 (OCH<sub>2</sub>), 99.4 (Cp), 100.1 (C4'), 103.6 (Co), 117.7 (C3), 120.4 (C5), 136.8 (Ci), 138.0 (C4), 149.3 (C3'), 150.2 (C5'), 151.1 (C6), 153.9 (C2), 160.2 (Cm).

[Pt(pz<sup>R(12,12)py</sup>)(pz<sup>R(10,10)py</sup>)] (20): red solid (28%). Found: C, 64.3; H, 7.9; N, 6.2. PtC<sub>72</sub>H<sub>108</sub>N<sub>6</sub>O<sub>4</sub>·0.3CHCl<sub>3</sub> requires C, 64.2; H, 8.1; N, 6.2%.  $\nu_{max}/\text{cm}^{-1}$ : 2925 – 2854s  $\nu(\text{C–H})_{\text{aliph}}$ , 1600s  $\nu(\text{C=C + C=N})$ , 756m  $\gamma(\text{C–H})_{\text{py}}$ .  $\delta_{\text{H}}$  (300.16 MHz; CDCl<sub>3</sub>; TMS): 0.88 (6H, m, CH<sub>3</sub>), 0.89 (6H, m, CH<sub>3</sub>), 1.28 (64H, m, CH<sub>2</sub>), 1.85 (8H, qt,  $^3J$  6.8, CH<sub>2</sub>), 4.04 (8H, t,  $^3J$  6.5, OCH<sub>2</sub>), 6.43 (2H, t,  $^4J$  2.0, Hp), 6.77 (2H, s, H4'), 7.02 (4H, d,  $^4J$  2.1, Ho), 7.13 (2H, pt,  $^3J$  6.5, H5), 7.46 (2H, d,  $^3J$  7.9, H3), 7.75 (2H, pt,  $^3J$  7.3, H4), 10.63 (2H, d,  $^3J$  5.5, H6).

[Pt(pz<sup>R(12,12)py</sup>)(pz<sup>R(14,14)py</sup>)] (21): red solid (31%). Found: C, 67.3; H, 8.6; N, 5.9. PtC<sub>80</sub>H<sub>124</sub>N<sub>6</sub>O<sub>4</sub> requires C, 67.2; H, 8.7; N, 5.9%.  $\nu_{max}/\text{cm}^{-1}$ : 2922 – 2850s  $\nu(\text{C–H})_{\text{aliph}}$ , 1597m  $\nu(\text{C=C + C=N})$ , 764w  $\gamma(\text{C–H})_{\text{py}}$ .  $\delta_{\text{H}}$  (300.16 MHz; CDCl<sub>3</sub>; TMS): 0.88 (12H, m, CH<sub>3</sub>), 1.26 (80H, m, CH<sub>2</sub>), 1.84 (8H, qt,  $^3J$  6.8, CH<sub>2</sub>), 4.05 (8H, t,  $^3J$  6.6, OCH<sub>2</sub>), 6.44 (2H, t,  $^4J$  2.0, Hp), 6.89 (2H, s, H4'), 7.09 (4H, d,  $^4J$  2.0, Ho), 7.26 (2H, m, H5), 7.59 (2H, d,  $^3J$  7.5, H3), 7.86 (2H, pt,  $^3J$  7.1, H4), 10.77 (2H, d,  $^3J$  5.5, H6).

**[Pt(pz<sup>R(12,12)py</sup>)(pz<sup>R(16,16)py</sup>)] (22):** red solid (27%). Found: C, 66.1; H, 8.5; N, 5.5. PtC<sub>84</sub>H<sub>132</sub>N<sub>6</sub>O<sub>4</sub>·0.4CHCl<sub>3</sub> requires C, 66.1; H, 8.7; N, 5.5%.  $\nu_{max}/\text{cm}^{-1}$ : 2922 – 2851s  $\nu(\text{C–H})_{\text{aliph}}$ , 1598m  $\nu(\text{C=C + C=N})$ , 764w  $\gamma(\text{C–H})_{\text{py}}$ .  $\delta_{\text{H}}$  (300.16 MHz; CDCl<sub>3</sub>; TMS): 0.87 (12H, t, <sup>3</sup>J 6.8, CH<sub>3</sub>), 1.26 (88H, m, CH<sub>2</sub>), 1.85 (8H, qt, <sup>3</sup>J 6.5, CH<sub>2</sub>), 4.05 (8H, t, <sup>3</sup>J 6.6, OCH<sub>2</sub>), 6.43 (2H, t, <sup>4</sup>J 2.1, Hp), 6.81 (2H, s, H4'), 7.06 (4H, d, <sup>4</sup>J 2.2, Ho), 7.16 (2H, ddd, <sup>3</sup>J 7.4, 5.9, <sup>4</sup>J 1.3, H5), 7.49 (2H, d, <sup>3</sup>J 7.7, H3), 7.76 (2H, ddd, <sup>3</sup>J 7.7, 7.7, <sup>4</sup>J 1.3, H4), 10.70 (2H, d, <sup>3</sup>J 5.6, H6).

**[Pt(pz<sup>R(12,12)py</sup>)(pz<sup>R(18,18)py</sup>)] (23):** red solid (38%). Found: C, 67.2; H, 8.7; N, 5.3. PtC<sub>88</sub>H<sub>140</sub>N<sub>6</sub>O<sub>4</sub>·0.3CHCl<sub>3</sub> requires C, 67.2; H, 9.0; N, 5.3%.  $\nu_{max}/\text{cm}^{-1}$ : 2924 – 2853s  $\nu(\text{C–H})_{\text{aliph}}$ , 1599m  $\nu(\text{C=C + C=N})$ , 758w  $\gamma(\text{C–H})_{\text{py}}$ .  $\delta_{\text{H}}$  (300.16 MHz; CDCl<sub>3</sub>; TMS): 0.87 (12H, t, <sup>3</sup>J 6.5, CH<sub>3</sub>), 1.25 (96H, m, CH<sub>2</sub>), 1.84 (8H, qt, <sup>3</sup>J 6.7, CH<sub>2</sub>), 4.04 (8H, t, <sup>3</sup>J 6.6, OCH<sub>2</sub>), 6.43 (2H, t, <sup>4</sup>J 2.1, Hp), 6.83 (2H, s, H4'), 7.05 (4H, d, <sup>4</sup>J 2.2, Ho), 7.20 (2H, ddd, <sup>3</sup>J 7.5, 5.9, <sup>4</sup>J 1.3, H5), 7.54 (2H, d, <sup>3</sup>J 7.7, H3), 7.76 (2H, ddd, <sup>3</sup>J 7.7, 7.7, <sup>4</sup>J 1.0, H4), 10.73 (2H, d, <sup>3</sup>J 5.6, H6).

### Compounds [Pt(pz<sup>R(12,12)iq</sup>)(pz<sup>R(n,n)iq</sup>)] 24-30

**[Pt(pz<sup>R(12,12)iq</sup>)(pz<sup>R(4,4)iq</sup>)] (24):** red solid (37%). Found: C, 63.6; H, 7.0; N, 6.4. PtC<sub>68</sub>H<sub>88</sub>N<sub>6</sub>O<sub>4</sub>·0.4CHCl<sub>3</sub> requires C, 63.6; H, 7.1; N, 6.5%.  $\nu_{max}/\text{cm}^{-1}$ : 2923 – 2853s  $\nu(\text{C–H})_{\text{aliph}}$ , 1640 – 1594s  $\nu(\text{C=C + C=N})$ , 772 – 718m  $\gamma(\text{C–H})_{\text{iq}}$ .  $\delta_{\text{H}}$  (300.16 MHz; CDCl<sub>3</sub>; TMS): 0.92 (6H, t, <sup>3</sup>J 6.9, CH<sub>3</sub>), 1.10 (6H, t, <sup>3</sup>J 7.2, CH<sub>3</sub>), 1.32 (40H, m, CH<sub>2</sub>), 1.84 (8H, qt, <sup>3</sup>J 6.7, CH<sub>2</sub>), 3.81 (4H, m, OCH<sub>2</sub>), 3.82 (4H, m, OCH<sub>2</sub>), 5.97 (2H, s, H4'), 6.25 (2H, br, Hp), 6.39 (4H, br, Ho), 6.85 (2H, s, H4), 7.07 (4H, m, H5, H7), 7.20 (2H, d, <sup>3</sup>J 7.4, H8), 7.40 (2H, pt, <sup>3</sup>J 6.8, H6), 10.57 (2H, s, H1).

**[Pt(pz<sup>R(12,12)iq</sup>)(pz<sup>R(6,6)iq</sup>)] (25):** red solid (33%). Found: C, 65.6; H, 7.2; N, 6.4. PtC<sub>72</sub>H<sub>96</sub>N<sub>6</sub>O<sub>4</sub>·0.1CHCl<sub>3</sub> requires C, 65.4; H, 7.5; N, 6.4%.  $\nu_{max}/\text{cm}^{-1}$ : 2920 – 2851s  $\nu(\text{C–H})_{\text{aliph}}$ , 1639 – 1594s  $\nu(\text{C=C + C=N})$ , 774 – 718m  $\gamma(\text{C–H})_{\text{iq}}$ .  $\delta_{\text{H}}$  (300.16 MHz; CDCl<sub>3</sub>; TMS): 0.92 (6H, t, <sup>3</sup>J 6.7, CH<sub>3</sub>), 1.00 (6H, t, <sup>3</sup>J 7.2, CH<sub>3</sub>), 1.33 (48H, m, CH<sub>2</sub>), 1.81 (8H, br, CH<sub>2</sub>), 3.76 (8H, br, OCH<sub>2</sub>), 5.87 (2H, s, H4'), 6.22 (2H, br, Hp), 6.35 (4H, br, Ho), 6.74 (2H, s, H4), 7.03 (4H, m, H5, H7), 7.10 (2H, br, H8), 7.37 (2H, br, H6), 10.50 (2H, s, H1).

**[Pt(pz<sup>R(12,12)iq</sup>)(pz<sup>R(8,8)iq</sup>)] (26):** red solid (38%). Found: C, 65.7; H, 7.4; N, 6.2. PtC<sub>76</sub>H<sub>104</sub>N<sub>6</sub>O<sub>4</sub>·0.3CHCl<sub>3</sub> requires C, 65.6; H, 7.5; N, 6.0%.  $\nu_{max}/\text{cm}^{-1}$ : 2920 – 2852s  $\nu(\text{C–H})_{\text{aliph}}$ , 1641 – 1594s  $\nu(\text{C=C + C=N})$ , 773 – 715m  $\gamma(\text{C–H})_{\text{iq}}$ .  $\delta_{\text{H}}$  (300.16 MHz; CDCl<sub>3</sub>; TMS): 0.91 (6H, t, <sup>3</sup>J 6.7 CH<sub>3</sub>), 0.95 (6H, t, <sup>3</sup>J 6.7, CH<sub>3</sub>), 1.31 (56H, m, CH<sub>2</sub>), 1.85 (8H, qt, <sup>3</sup>J 6.5, CH<sub>2</sub>), 3.85 (8H, t, <sup>3</sup>J 6.4, OCH<sub>2</sub>), 6.09 (2H, s, H4'), 6.28 (2H, br, Hp), 6.50 (4H, br, Ho), 6.95 (2H, s, H4), 7.16 (4H, m, H5, H7), 7.30 (2H, m, H8), 7.46 (2H, pt, <sup>3</sup>J 6.5, H6), 10.74 (2H, s, H1).  $\delta_{\text{C}}$  (75.48 MHz; CDCl<sub>3</sub>; TMS): 14.4 (CH<sub>3</sub>), 23.0 – 32.3 (CH<sub>2</sub>), 67.9 (OCH<sub>2</sub>), 98.3 (C4'), 99.5 (Cp), 102.2 (Co), 113.4 (C4), 126.0 (C10), 126.0 (C7), 126.5 (C5), 128.5 (C8), 131.5 (C6), 135.9 (C9), 136.8 (Ci), 146.4 (C3), 148.4 (C3'), 150.0 (C5'), 155.3 (C1), 160.0 (Cm).

**[Pt(pz<sup>R(12,12)iq</sup>)(pz<sup>R(10,10)iq</sup>)] (27):** red solid (47%). Found: C, 66.3; H, 7.7; N, 5.7. PtC<sub>80</sub>H<sub>112</sub>N<sub>6</sub>O<sub>4</sub>·0.3CHCl<sub>3</sub> requires C, 66.4; H, 7.8; N, 5.8%.  $\nu_{\text{max}}/\text{cm}^{-1}$ : 2918 – 2851s  $\nu(\text{C–H})_{\text{aliph}}$ , 1641 – 1593s  $\nu(\text{C=C} + \text{C=N})$ , 774 – 717m  $\gamma(\text{C–H})_{\text{iq}}$ .  $\delta_{\text{H}}$  (300.16 MHz; CDCl<sub>3</sub>; TMS): 0.90 (6H, t, <sup>3</sup>J 6.7 CH<sub>3</sub>), 0.92 (6H, t, <sup>3</sup>J 6.9, CH<sub>3</sub>), 1.31 (64H, m, CH<sub>2</sub>), 1.89 (8H, qt, <sup>3</sup>J 6.6, CH<sub>2</sub>), 3.94 (8H, t, <sup>3</sup>J 6.4, OCH<sub>2</sub>), 6.34 (4H, m, Hp, H4'), 6.68 (4H, br, Ho), 7.20 (2H, s, H4), 7.26 (4H, m, H5, H7), 7.55 (4H, m, H6, H8), 11.00 (2H, s, H1).

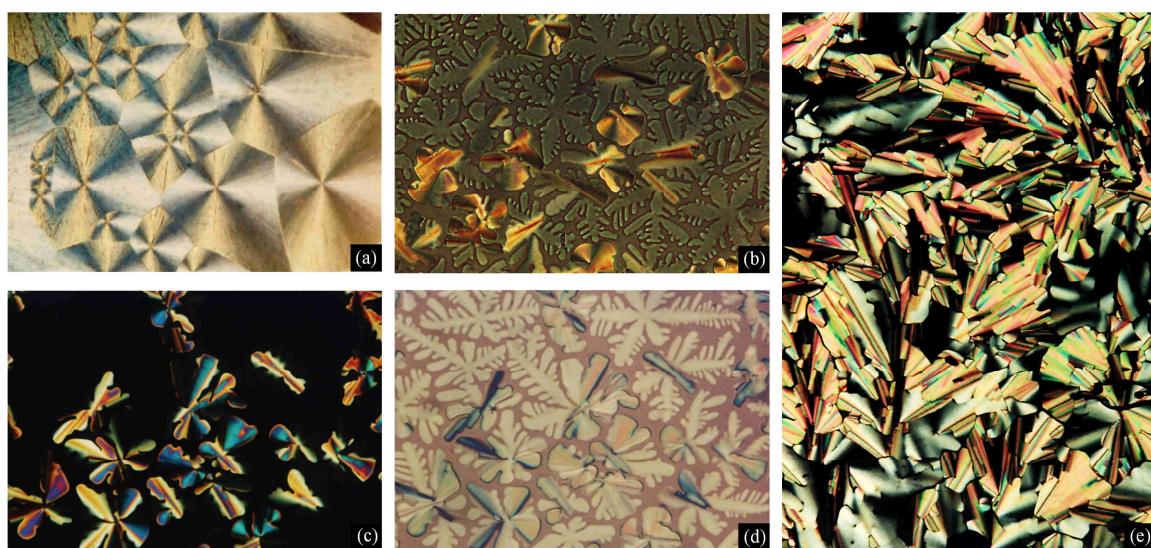
**[Pt(pz<sup>R(12,12)iq</sup>)(pz<sup>R(14,14)iq</sup>)] (28):** red solid (47%). Found: C, 68.1; H, 8.2; N, 5.2. PtC<sub>88</sub>H<sub>128</sub>N<sub>6</sub>O<sub>4</sub>·0.2CHCl<sub>3</sub> requires C, 68.2; H, 8.3; N, 5.4%.  $\nu_{\text{max}}/\text{cm}^{-1}$ : 2921 – 2852s  $\nu(\text{C–H})_{\text{aliph}}$ , 1639 – 1593s  $\nu(\text{C=C} + \text{C=N})$ , 768 – 712m  $\gamma(\text{C–H})_{\text{iq}}$ .  $\delta_{\text{H}}$  (300.16 MHz; CDCl<sub>3</sub>; TMS): 0.89 (12H, m, CH<sub>3</sub>), 1.30 (80H, m, CH<sub>2</sub>), 1.83 (8H, br, CH<sub>2</sub>), 3.84 (8H, br, OCH<sub>2</sub>), 6.20 (2H, br, H4'), 6.28 (2H, br, Hp), 6.54 (4H, br, Ho), 7.06 (2H, br, H4), 7.19 (4H, m, H5, H7), 7.26 (2H, m, H8), 7.47 (2H, br, H6), 10.73 (2H, br, H1).

**[Pt(pz<sup>R(12,12)iq</sup>)(pz<sup>R(16,16)iq</sup>)] (29):** red solid (41%). Found: C, 69.1; H, 8.5; N, 4.7. PtC<sub>92</sub>H<sub>136</sub>N<sub>6</sub>O<sub>4</sub>·0.2CHCl<sub>3</sub> requires C, 68.8; H, 8.5; N, 5.2%.  $\nu_{\text{max}}/\text{cm}^{-1}$ : 2917 – 2850s  $\nu(\text{C–H})_{\text{aliph}}$ , 1641 – 1594s  $\nu(\text{C=C} + \text{C=N})$ , 775 – 718m  $\gamma(\text{C–H})_{\text{iq}}$ .  $\delta_{\text{H}}$  (300.16 MHz; CDCl<sub>3</sub>; TMS): 0.90 (6H, m, CH<sub>3</sub>), 0.92 (6H, m, CH<sub>3</sub>), 1.32 (88H, m, CH<sub>2</sub>), 1.84 (8H, br, CH<sub>2</sub>), 3.80 (8H, br, OCH<sub>2</sub>), 5.95 (2H, s, H4'), 6.25 (2H, br, Hp), 6.41 (4H, br, Ho), 6.84 (2H, s, H4), 7.10 (4H, m, H5, H7), 7.18 (2H, d, <sup>3</sup>J 7.8, H8), 7.41 (2H, pt, <sup>3</sup>J 6.7, H6), 10.59 (2H, s, H1).

**[Pt(pz<sup>R(12,12)iq</sup>)(pz<sup>R(18,18)iq</sup>)] (30):** red solid (37%). Found: C, 69.4; H, 8.4; N, 5.0. PtC<sub>96</sub>H<sub>144</sub>N<sub>6</sub>O<sub>4</sub>·0.2CHCl<sub>3</sub> requires C, 69.4; H, 8.7; N, 5.0%.  $\nu_{\text{max}}/\text{cm}^{-1}$ : 2924 – 2851s  $\nu(\text{C–H})_{\text{aliph}}$ , 1641 – 1594s  $\nu(\text{C=C} + \text{C=N})$ , 776 – 718m  $\gamma(\text{C–H})_{\text{iq}}$ .  $\delta_{\text{H}}$  (300.16 MHz; CDCl<sub>3</sub>; TMS): 0.89 (6H, t, <sup>3</sup>J 6.8, CH<sub>3</sub>), 0.92 (6H, t, <sup>3</sup>J 6.5, CH<sub>3</sub>), 1.28 (96H, m, CH<sub>2</sub>), 1.84 (8H, br, CH<sub>2</sub>), 3.82 (8H, br, OCH<sub>2</sub>), 6.06 (2H, s, H4'), 6.27 (2H, br, Hp), 6.47 (4H, br, Ho), 6.94 (2H, s, H4), 7.14 (4H, m, H5, H7), 7.14 (2H, m, H8), 7.44 (2H, br, H6), 10.67 (2H, s, H1).

**Table S1.** Selected bond distances and angles for [PtCl<sub>2</sub>(Hpz<sup>R(6,6)py</sup>)]·CH<sub>3</sub>CN·H<sub>2</sub>O (**2**·CH<sub>3</sub>CN·H<sub>2</sub>O)

Bond distances [ $\text{\AA}$ ]		Bond angles [ $^{\circ}$ ]	
Pt–N1	1.999(5)	N1–Pt–N3	80.4(2)
Pt–N3	2.024(6)	N1–Pt–Cl2	173.9(2)
Pt–Cl1	2.308(3)	N1–Pt–Cl1	97.3(2)
Pt–Cl2	2.281(3)	N3–Pt–Cl2	93.6(2)
		N3–Pt–Cl1	177.0(2)
		Cl1–Pt–Cl2	88.7(1)



**Figure S1.** POM images of the columnar mesophases of (a)  $[\text{PtCl}_2(\text{Hpz}^{\text{R}(14,14)\text{py}})]$  **6** at 121 °C, (b)  $[\text{Pt}(\text{pz}^{\text{R}(12,12)\text{py}})(\text{pz}^{\text{R}(18,18)\text{py}})]$  **23** at 134 °C, (c,d)  $[\text{Pt}(\text{pz}^{\text{R}(12,12)\text{iq}})(\text{pz}^{\text{R}(8,8)\text{iq}})]$  **26** at 306 °C, and (e)  $[\text{Pt}(\text{pz}^{\text{R}(12,12)\text{iq}})(\text{pz}^{\text{R}(10,10)\text{iq}})]$  **27** at 308 °C, on cooling. All microphotographs were taken under crossed polarizers, except (b) and (d).

**Table S2.** Thermal behavior of the pyridylpyrazole Pt(II) dichloride compounds  $[\text{PtCl}_2(\text{Hpz}^{\text{R}(n,n)\text{py}})]$  **1-8**

n		Transition <sup>[a]</sup>	T [°C] ( $\Delta H [\text{kJ mol}^{-1}]$ ) <sup>b</sup>	n		Transition <sup>a</sup>	T [°C] ( $\Delta H [\text{kJ mol}^{-1}]$ ) <sup>b</sup>
4	<b>1</b>	Cr→I	231 (22.8) <sup>c</sup>	12	<b>5</b>	Cr→Cr'→Col <sub>L</sub> →I	49 (5.2), 96 (28.3), 166 (11.8)
		I→Cr	178 <sup>d</sup>			I→Col <sub>L</sub> →Cr	140 <sup>d</sup> , 80 <sup>d</sup>
6	<b>2</b>	Cr→I	206 <sup>c,d</sup>	14	<b>6</b>	Cr→Cr'→Col <sub>L</sub> →I	48 (8.6), 98 (22.3), 159 (5.8)
		I→Cr	202 <sup>d</sup>			I→Col <sub>L</sub> →Cr	141 <sup>d</sup> , 70 <sup>d</sup>
8	<b>3</b>	Cr→I	194 (20.0)	16	<b>7</b>	Cr→Cr'→Col <sub>L</sub> →I	58 (6.3), 105 (32.3), 151 (7.4)
		I→Cr	167 (-19.0)			I→Col <sub>L</sub> →Cr	144 <sup>d</sup> , 71 <sup>d</sup>
10	<b>4</b>	Cr→I	172 (12.9)	18	<b>8</b>	Cr→Cr'→Col <sub>L</sub> →I	49 (15.2), 109 (17.8), 124 (3.7) <sup>e</sup>
		I→Cr	137 (-5.7)				

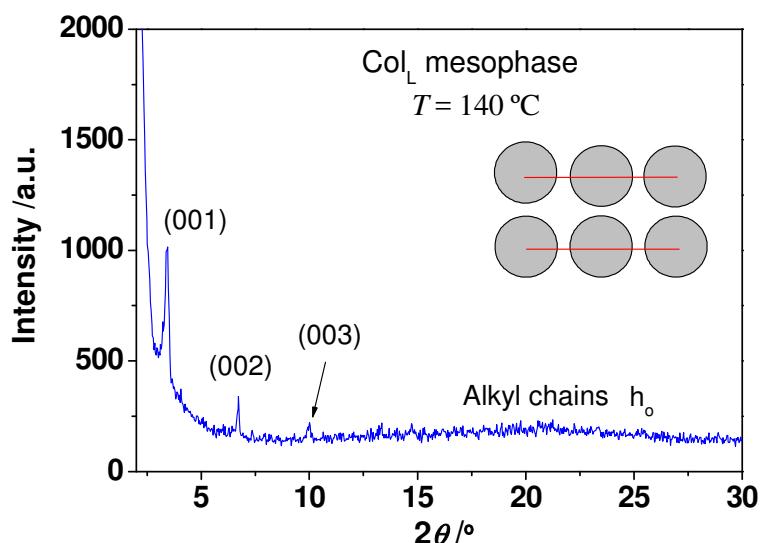
<sup>a</sup> Cr, Cr' = crystalline phases, Col<sub>L</sub> = lamellar columnar mesophase, I = isotropic liquid. <sup>b</sup> DSC onset peaks. <sup>c</sup> Partial decomposition. <sup>d</sup> Detected by POM. <sup>e</sup> Pronounced decomposition.

**Table S3.** Thermal behavior of isoquinolinylpyrazole Pt(II) dichloride compounds  $[\text{PtCl}_2(\text{Hpz}^{\text{R}(n,n)\text{iq}})]$  **9-16**

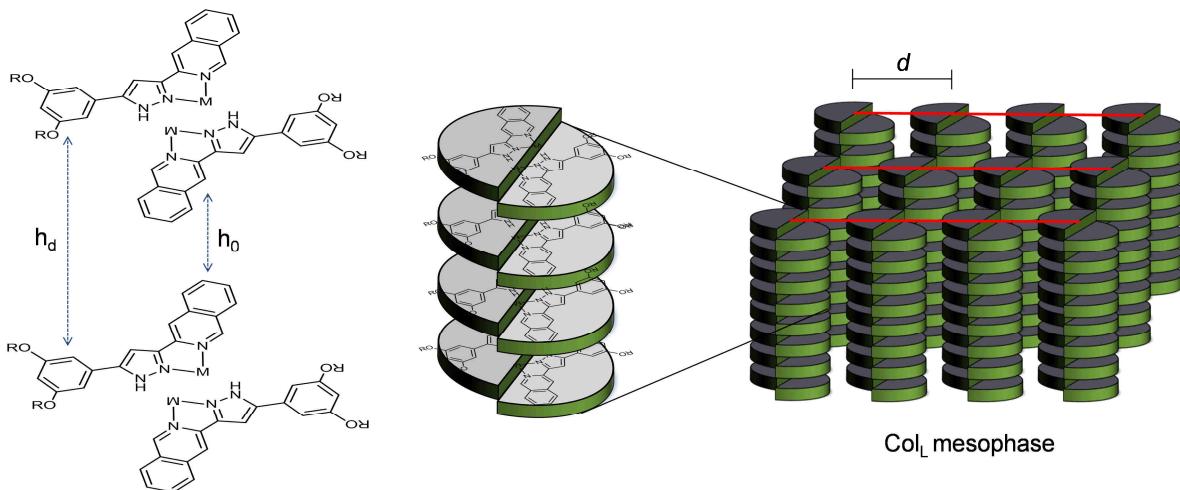
n		Transition <sup>a</sup>	T [°C] ( $\Delta H [\text{kJ mol}^{-1}]$ ) <sup>b</sup>	n		Transition <sup>a</sup>	T [°C] ( $\Delta H [\text{kJ mol}^{-1}]$ ) <sup>b</sup>
4	<b>9</b>	Cr→I	300 <sup>c</sup>	12	<b>13</b>	Cr→Cr'→Col <sub>L</sub> →I	77 (1.3), 86 (1.5), 224 <sup>d</sup>
6	<b>10</b>	Cr→I	267 <sup>d</sup>	14	<b>14</b>	Cr→Cr'→Col <sub>L</sub> →I	60 (24.2) <sup>e</sup> , 217 <sup>d</sup>
8	<b>11</b>	Cr→I	267 <sup>d</sup>	16	<b>15</b>	Cr→Cr'→Col <sub>L</sub> →I	50 (6.7), 68 (7.6), 214 <sup>d</sup>
10	<b>12</b>	Cr→I	250 <sup>d</sup>	18	<b>16</b>	Cr→Cr'→Col <sub>L</sub> →I	52 (5.0), 80 (29.5), 205 <sup>d</sup>

<sup>a</sup> Cr, Cr' = crystalline phases, Col<sub>L</sub> = lamellar columnar mesophase, I = isotropic liquid. <sup>b</sup> DSC onset peaks.

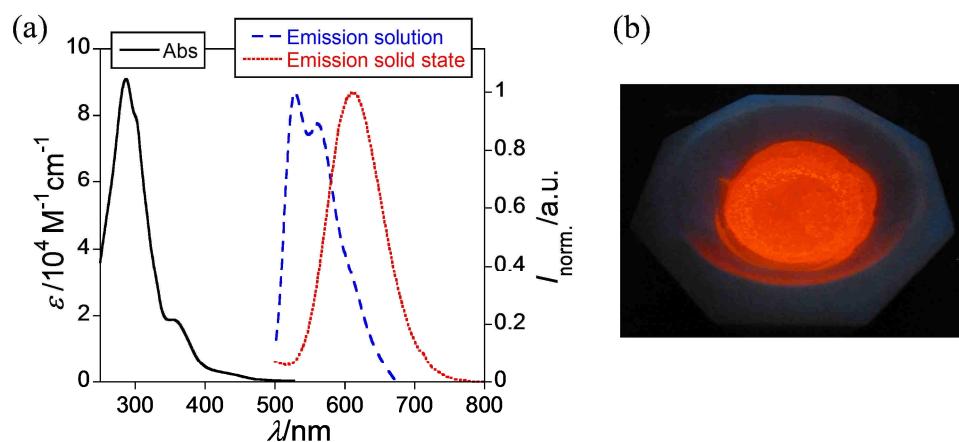
<sup>c</sup> Detected by POM. <sup>d</sup> Enthalpy was not determined due to pronounced decomposition. <sup>e</sup> Overlapped processes.



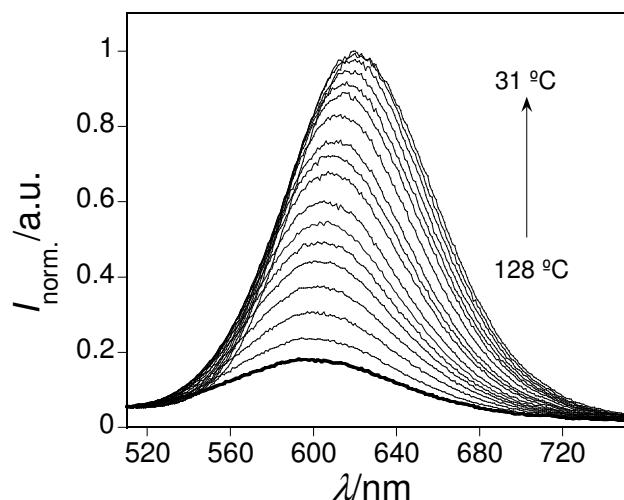
**Figure S2.** X-ray diffractogram for compound  $[\text{PtCl}_2(\text{Hpz}^{\text{R}(12,12)\text{py}})]$  **5** recorded at 140 °C on heating



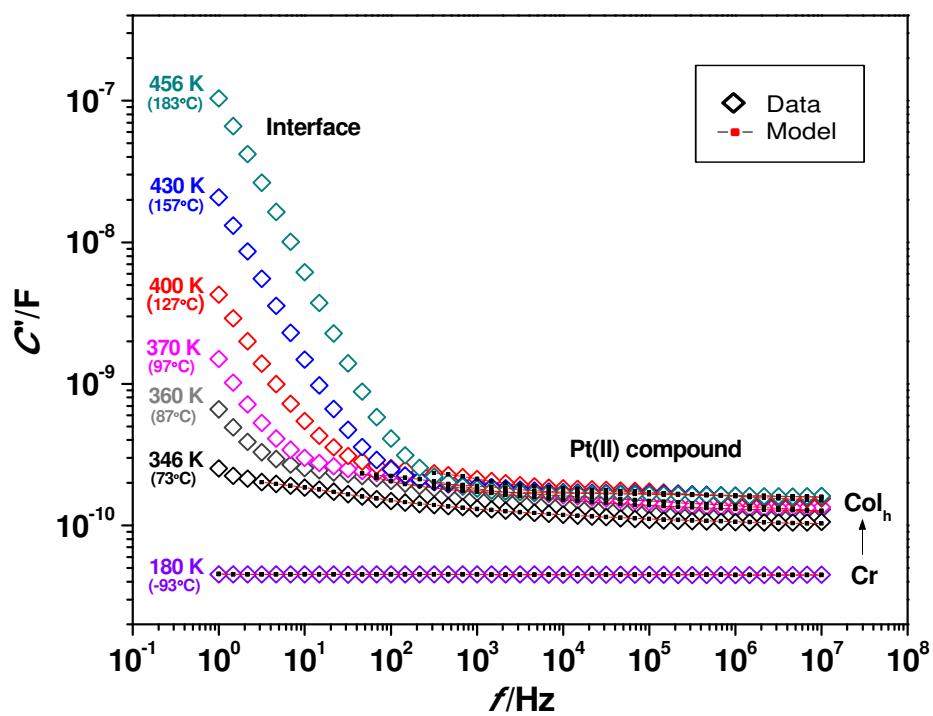
**Figure S3.** Proposed schematic model for the  $\text{Col}_L$  mesophase of the Pt(II) dichloride compounds ( $M = \text{Pt}$ ,  $R = \text{C}_n\text{H}_{2n+1}$ ,  $n = 12-18$ ). Dichloride atoms have been omitted for the sake of clarity.



**Figure S4.** (a) UV-vis absorption and normalized emission spectra in solution in  $\text{CH}_2\text{Cl}_2$  ( $1.0 \times 10^{-5} \text{ M}$ ) and in the solid state for the asymmetrical Pt(II) compound  $[\text{Pt}(\text{pz}^{\text{R}(12,12)\text{iq}})(\text{pz}^{\text{R}(6,6)\text{iq}})]$  **25**. (b) Image of the luminescence emission of  $[\text{Pt}(\text{pz}^{\text{R}(12,12)\text{iq}})(\text{pz}^{\text{R}(14,14)\text{iq}})]$  **28** taken in the solid state at room temperature under UV radiation ( $\lambda = 365 \text{ nm}$ ).



**Figure S5.** Normalized emission spectra of  $[\text{Pt}(\text{pz}^{\text{R}(12,12)\text{py}})(\text{pz}^{\text{R}(4,4)\text{py}})]$  **17** as a function of temperature upon cooling.



**Figure S6.** Capacitance ( $C$ ) of compound  $[\text{Pt}(\text{pz}^{\text{R}(12,12)\text{py}})(\text{pz}^{\text{R}(18,18)\text{py}})]$  **23** as a function of frequency ( $f$ ) at selected temperatures. The solid (Cr) – mesophase (Col<sub>h</sub>) transition is indicated.