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# Synthesis and Crystal Packing of *trans*-Bis(2aminotroponato)palladium(II) Complexes Bearing Linear Alkyl Chains – Hard Lamellar Structures Self-Locked by Cross-Shaped Molecular Units

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The synthesis, structure, and three-dimensional lamellar array of a series of *trans*-bis(2-aminotroponato- $\kappa N, \kappa O$ )palladium(II) complexes bearing linear alkyl chains (**1a**: n = 5; **1b**: n = 8; **1c**: n = 14; **1d**: n = 16; **1e**: n = 18, where n is the number of carbon atoms in the chain) attached to *trans* nitrogen donor atoms are described. The *trans*-coordination of the ligands, the cross-shaped molecular structures, and the crystal packing of **1b** and **1c** have been unequivocally established from single-crystal XRD studies. Highly regulated multilayered lamellar structures are observed for **1b** and **1c**, where every lamellar layer in the crystallographic *ab* plane, formed by  $\pi$ -stacking interactions of metal cores and van der Waals

# Introduction

The elucidation and application of lamellar arrangements of linear chain molecules are important for the development of new materials whose functions rely on molecular aggregation. Lamellar crystals have been studied in order to investigate the higher order structures of various polymers such as paraffins,<sup>[1]</sup> polyolefins,<sup>[2]</sup> polyamides,<sup>[3]</sup> polyurethanes,<sup>[4]</sup> and polyesters.<sup>[5]</sup> In the fields of inorganic and organometallic chemistry, similar layered structures have been extensively studied using transition metal complexes bearing long alkyl chains, with the aim of achieving liquid crystalline properties. A variety of transition metal complexes bearing square-planar coordination sites to which long alkyl chains are appended have been reported to act as efficient mesogens.<sup>[6]</sup> These complexes typically have long, rod-like molecular shapes due to pairs of trans-disposed linear alkyl chains along the axial direction of the molecule. This characteristic molecular shape generates a moderate balance of molecular mobility and rigidity in the

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interactions between alkyl chains, is laminated alternately on the *c* axis with an orthogonal lamellar array of the identical unit. Powder XRD analysis showed that **1b–1e** exhibit diffraction peaks attributed to periodic (*n*00) reflections of a typical lamellar structure. A linear correlation between the *d*-spacing and chain lengths in these compounds indicates that they form the same type of three-dimensional layer-by-layer structure of lamellar aggregates. The correlation between the cross-shaped molecular structures of **1b–1e** and the dimensionality of molecular constraint in the crystal packing is discussed by comparison with those of rod-shaped analogues that exhibit high liquid crystallinity.

condensed state, due to the low-dimensional aggregation properties. In contrast to the soft lamellar structures of the above complexes, hard lamellar crystals have been reported to form in the limited cases of less planar, long-chained complexes such as ferrocene,<sup>[7]</sup> [Cu(OSO<sub>2</sub>R)<sub>2</sub>],<sup>[8]</sup> [Cu<sub>2</sub>-(OCOR)<sub>4</sub>],<sup>[9]</sup> [Zn<sub>2</sub>(OAc)<sub>4</sub>(tpy–OR)<sub>2</sub>],<sup>[10]</sup> and [AgBr<sub>2</sub>-(NHCR)<sub>2</sub>] (NHC: N-heterocyclic carbene).<sup>[11]</sup>

Hard lamellar crystals of diads comprising transition metals and alkyl chains could potentially express a variety of photoelectric properties upon morphological control of the functional metal cores, although, in contrast to extensive studies on the liquid crystalline properties of soft lamellar structures, this has not yet been investigated.<sup>[6]</sup> As part of our program aimed at developing new functionalities of square-planar d<sup>8</sup> transition metal complexes,<sup>[12]</sup> we recently showed that typically nonemissive crystals of trans-bis(salicylaldiminato)platinum(II) complexes bearing long alkyl chains can be changed to highly emissive crystals by morphological control of the lamellar structure through crystal engineering.<sup>[13]</sup> This result indicates that an understanding of the correlation between lamellar structures and the shape of molecular units can aid in the design of future photoelectric devices. In this paper, we investigate the molecular arrays formed by *trans*-bis(2-aminotroponato- $\kappa N, \kappa O$ )palladium(II) complexes (1) bearing long alkyl chains attached to trans nitrogen donor atoms in the crystalline state

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(Scheme 1).<sup>[14]</sup> Unlike the rod-shaped (alkoxytroponato)metal analogues,<sup>[14f,15]</sup> cross-shaped complexes **1** with "horizontal" alkyl chains form hard lamellar crystals with nonmesogenic properties. Single-crystal XRD analyses of **1b** and **1c**, and powder XRD analyses of **1a–1e**, show that **1b–1e** consist of characteristic multilayered lamellar structures, where each lamellar layer is laminated alternately with another identical lamellar layer rotated by 180°.



Scheme 1.

Both the structure and crystal packing show that high dimensionality in self-constrained molecular units can be attributed to the specific anisotropy of the intermolecular interactions, which results from the cross-shaped structures of **1b–1e**. Recently we reported that the self-constraint of molecular units in the condensed state is one of the major controlling factors in the intense solid-state phosphores-cence of platinum complexes.<sup>[12b–12e,13]</sup> The present results provide significant information regarding the correlation between molecular shape and self-constraint of the molecular units in crystals, which will aid in the design of hard and soft matter with excellent photoelectric properties.

## **Results and Discussion**

#### Synthesis and Characterization of 1

The *trans*-bis(aminotroponato- $\kappa N, \kappa O$ )palladium(II) complexes **1a–1e**, bearing linear alkyl chains (**1a**: n = 5; **1b**: n = 8; **1c**: n = 14; **1d**: n = 16; **1e**: n = 18, where n is the number of carbon atoms in the chain) were synthesized by the reaction of [Pd(OAc)<sub>2</sub>] with the corresponding 2-(alkylamino)tropone in the presence of N, N, N', N'-tetramethylethylenediamine in refluxing toluene at reflux. The 2-(alkylamino)tropones were prepared by reaction of tropolone with SOCl<sub>2</sub> and subsequent amination of the resulting chloride.<sup>[16]</sup> Complexes **1a–1e** were characterized using <sup>1</sup>H NMR, <sup>13</sup>C NMR (Figures S1–S5, Supporting Information), and FTIR spectroscopy, and high-resolution mass spectrometry. The *trans* disposition of the alkyl groups in **1b** and **1c** has been unequivocally established by single-crystal XRD (Table 1). ORTEP drawings of **1b** and **1c** are shown in Figures 1 and 2. The tropone rings, ligand donor atoms, and metal ion are essentially coplanar, as indicated by the small dihedral angles between the coordination plane [Pd1–

Table 1. Crystal data and structure refinement details for compounds 1b and 1c.

	1b	1c
Formula	C <sub>30</sub> H <sub>44</sub> N <sub>2</sub> O <sub>2</sub> Pd	C42H68N2O2Pd
Formula weight	571.09	739.41
Temperature /K	113	113
Crystal color, habit	red, platelets	red, platelets
Crystal size /mm	$0.60 \times 0.20 \times 0.04$	$0.24 \times 0.12 \times 0.04$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$ (#14)	$P2_1/c$ (#14)
a /Å	14.963(3)	22.083(2)
b /Å	5.0165(8)	4.9812(3)
c /Å	18.774(4)	17.903(1)
a /°	90	90
β /°	96.808(5)	95.354(2)
γ /°	90	90
$V/Å^3$	1399.2(4)	1960.7(2)
Ζ	2	2
$D_{\rm calcd.}$ /g cm <sup>-3</sup>	1.355	1.252
$\mu$ (Mo- $K_{\alpha}$ ) /cm <sup>-1</sup>	6.918	5.093
<i>F</i> (000)	600.00	792.00
$2\theta_{\rm max}$ /°	55.0	54.9
No. of reflns. measd.	24278	38387
No. of obsd. reflns.	3195	4467
No. of variables	248	215
$R_1 [I > 2\sigma(I)]^{[a]}$	0.055	0.064
$wR_2$ (all reflns.) <sup>[b]</sup>	0.168	0.168
Goodness of fit	1.19	1.15

[a] 
$$R_1 = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$$
. [b]  $wR_2 = {\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2}^{1/2}$ .



Figure 1. ORTEP drawing of **1b**. (a) Top and (b) side views [C5–C5' projection]. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (in Å) and angles (in °): Pd1–O1 1.986(3), Pd1–N1 1.977(4), O1–C1 1.305(6), N1–C2 1.324(6); O1–Pd1–N1 80.40(13), O1–Pd1–N1' 99.60(13), O1–Pd1–N1–C2 1.7(3), N1–Pd1–O1–C1 0.3(2).





Figure 2. ORTEP drawing of 1c. (a) Top and (b) side views [C5–C5' projection]. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (in Å) and angles (in °): Pd1–O1 1.985(3), Pd1–N1 1.979(4), O1–C1 1.301(6), N1–C2 1.334(6); O1–Pd1–N1 80.55(14), O1–Pd1–N1' 99.45(14), O1–Pd1–N1–C2 1.6(2), N1–Pd1–O1–C1 1.9(2).

O1-N1] and the tropone ring [C1-C3-C5] (2.50° 1b, 1.22° 1c) as well as the small [C1-C2-N1-Pd1] (2.69° 1b, 1.21° 1c) and [C2-C1-O1-Pd1] (1.10° 1b, 1.76° 1c) torsion angles. Intramolecular H-bonding interactions between O1 and H8' are observed, with distances of 2.54 (for 1b) and 2.58 (for 1c) Å. The characteristic conformation observed for both 1b and 1c, where horizontal alkyl chains extend above and below the square plane, (Figures 1b and 2b), is noteworthy. As discussed later, such a conformation induces high dimensionality with significant intermolecular constraint of the crystals. Complexes 1b-1e immediately form platelet crystals when hot solutions in various solvents such as cyclohexane, benzene, toluene, EtOAc, and THF are cooled to room temperature. Scanning electron microscopy (SEM) images of microcrystalline 1c and 1e obtained from EtOAc are shown in Figure 3. Differential scanning calorimetry (DSC) analysis (Figure S6, Supporting Information) and polarized microscopy observations indicate that complexes **1a–1e** do not exhibit mesophases.



Figure 3. SEM images of microcrystalline (a) 1c and (b) 1e obtained by crystallization from hot EtOAc solution.

#### XRD Studies on Lamellar Crystals 1

Packing diagrams of 1b and 1c are shown in Figure 4. The most important features evident in these diagrams are the multilayered lamellar motifs, which are supported by  $\pi$ -stacking interactions between the planar regions of the complexes, and van der Waals forces between the linear alkyl chains. Single-layered lamellar structures viewed down the c axis are shown in Figure 4a and 4d, where the *trans*bis(2-aminotroponato)Pd unit of each molecule is aligned along the crystallographic b axis on the ab plane, giving  $\pi$ stacking interactions with distances of 3.50 Å (for 1b) and 3.48 Å (for 1c). Alkyl chains are aligned in a highly linear manner with a typical zigzag conformation, assisted by van der Waals interactions between neighboring cofacial molecular units. Note that every lamellar layer in the ab plane is laminated alternately along the c axis with another lamellar layer, where each molecular unit is identical, but rotated 180° about the c axis [symmetry code: (-x, 1/2 + y, 1/2 - z), (x, 1/2 - y, 1/2 + z)]. Such a characteristic layerby-layer structure, which consists of alternate stacking of orthogonal arrays of each unit, can be visualized by viewing down the c axis (Figure 4b, e) or b axis (Figure 4c, f). Closeup views of adjacent stacked pairs of 1b and 1c molecules (Figure 5a, b) indicate that each molecular unit undergoes typical offset stacking between O1 and the C3-C4-C5 plane of the tropone ring. The contribution of the "2-aminotropone" form is greater than that of the "2-hydroxytropone imine" form in (2-aminotroponato)metal complexes,<sup>[14d]</sup> so that the offset stacking shown in Figure 5 is attributed to a donor-acceptor interaction between the electron-deficient





Figure 4. Packing of (a–c) **1b** and (d–f) **1c**. (a,d) Single-layered lamellar structures in the *ab* plane (*c* axis projection). (b,e) Multilayered lamellar structures in the *ab* plane (*c* axis projection), and (c,f) side views in the *ac* plane (*b* axis projection). Molecular units in the upper and lower layers of the *ab* plane are colored orange. Hydrogen atoms are omitted for clarity.

carbonyl [C1–O1] and electron-rich 1,3-dienamine [N1–C2–C3–C4–C5] moieties of the tropone rings. The coordination planes on each layer are hydrogen-bonded to each other through the O1 and H6 atoms of the tropone ring, as shown in Figure 5c and 5d, which means that each lamellar layer experiences both intermolecular hydrogen-bonding and van der Waals interactions to form the multilayered lamellar structure.

Powder XRD patterns of 1b-1e (n = 8-18) show a series of sharp diffraction peaks attributable to the typical lamellar reflection of a multilayered structure, while the pattern of 1a, which contains shorter chains, (n = 5) is different (Figure 6). Layer spacings (d-spacings) for 1b (15.2 Å) and 1c (22.5 Å) are in accordance with the *a* axis lengths of each unit cell (15.0 Å, 22.1 Å), which indicates that the major peaks in these XRD patterns are due to the (100), (200), and (300) reflections. Figure 7 shows the correlation between chain length (n) and d-spacing estimated by indexing the diffraction peaks of the (100) reflections. The d-spacings of 1b-1e increase essentially proportionally to the chain lengths ( $R^2 = 0.999$ ); however, that of **1a** is much longer than that expected from this relationship. These results indicate that 1b-1e, which contain long alkyl chains, have similar multilayered lamellar structures, while 1a forms a nonlamellar packing motif.



Figure 5. Major interactions between the coordination planes in crystals of (a,c) **1b** and (b,d) **1c**. (a,b) Offset  $\pi$ -stacking interaction in the single lamellar layer. (c,d) Interlayer hydrogen-bonding interaction. Molecular units in the upper layer of the *ab* plane are colored orange.





Figure 6. XRD patterns for crystals of (a) 1a, (b) 1b, (c) 1c, (d) 1d, and (e) 1e. The calculated interlayer spacings from the (100) reflections are listed in each pattern.



Figure 7. Correlation between chain length (*n*) and interlayer spacings (*d*-spacings) in **1a–1e**.

#### Molecular Mobility of Cross- and Rod-Shaped Molecules in the Lamellar Arrangement

The correlation between the molecular shape and lamellar structure for typical cross- and rod-shaped molecules is shown in Figure 8. Cross-shaped complexes **1b–1e** form hard lamellar structures that are not liquid crystals. This is in contrast to the rod-shaped, square-planar complexes bearing *trans*-bis(5-alkoxy-2-aminotroponato)<sup>[14f]</sup> and bis(4-alkoxytroponato)<sup>[15]</sup> ligands, which form low-dimensional

soft lamellar structures that exhibit high mesogenic properties. This can be rationalized by assuming anisotropy in both the  $\pi$ -stacking and van der Waals interactions of these molecular units in lamellar aggregates. Both of the crossand rod-shaped units form layer-by-layer lamellar structures upon molecular aggregation. Each molecular unit experiences consecutive  $\pi$ -stacking interactions between the coordination planes and van der Waals forces between long alkyl chains to form a single-layered lamellar structure, which becomes increasingly multistratified, mainly as a result of the van der Waals forces between the alkyl chains. Assuming that the most efficient direction for molecular mobility in the crystals is perpendicular to the direction of the axis for consecutive stacking and van der Waals interactions, then the direction of molecular mobility to break the  $\pi$ -stacking interactions in **1b–1e** is perpendicular to that needed for breaking the van der Waals interactions in single-layered lamellar arrays (Figure 8a). As shown in the packing of 1b and 1c (Figure 4b, e), this single layer is laminated to afford the multilayered lamellar structure in an alternate manner, where the upper identical lamellar layer of 1b and 1c units is situated orthogonally over the original layer to maximize the interlayer interactions. Thus, the direction of molecular mobility to unlock the  $\pi$ -stacking interaction between molecular units on the lower horizontal single lamellar layer should be perpendicular to that on the upper layer. This means that three-dimensional molecular mobility is required to unlock the overall self-constraint in the crystal packing of the cross-shaped molecules 1b-1e.

In contrast to complexes **1b–1e**, the molecular constraint of rod-shaped complexes with high mesogenic properties is



Figure 8. Schematic representation of morphological differences in lamellar aggregates of square-planar metal complexes bearing long alkyl chains. Arrows denote the direction of molecular mobility required to break  $\pi$ -stacking (red) and van der Waals (blue) interactions.

quite homogeneous, as indicated by the highly regulated lamellar packing of the mesogenic bis(4-hexadecyloxytroponato)copper(II) complex<sup>[15b]</sup> shown in Figure 8b. As a corollary of the rod-shaped molecular structure, the direction of molecular mobility to cleave  $\pi$ -stacking interactions is the same as that needed to cleave the van der Waals interactions between alkyl chains in a single lamellar layer. The overall direction for breaking the interactions is not changed in the multilayered structure, because the upper single lamellar layer is identical to the neighboring layers in this case. This simple dimensionality in molecular constraint is the key to high mobility, that is, the low self-constraint of rod-shaped molecular units in a condensed system. Figure 4 and Figure 5 show that the significant interlayer interactions in 1b and 1c are limited to van der Waals interactions between alkyl chains and hydrogen bonding between the coordination planes. There is no significant  $\pi$ stacking and CH– $\pi$  contact in the interlayer interactions. Therefore, the overall interlayer interactions in the crossshaped complex crystals are not significantly greater than those of the rod-shaped analogues. Thus, it is fairly certain that the rigidity of the cross-shaped molecular units in the lamellar arrangement is not due to the total strength of intermolecular interactions, but is rather a result of the high dimensionality in molecular mobility required to break the interactions.

# Conclusions

A series of cross-shaped complexes based on *trans*-bis(2aminotroponato)palladium(II), and bearing long alkyl chains, was synthesized. These complexes form hard lamellar crystals, in contrast to the typical rod-shaped analogues of metallomesogens. Single-crystal and powder XRD analyses revealed that anisotropic intermolecular interactions specifically arising from cross-shaped molecular units is the key to high molecular constraint within the threedimensional, hard lamellar structure of **1b–1e**. Morphological control to enhance self-constraint of molecular aggregates will be important to avoid dispersion of photon energy in the development of future light-emitting devices.<sup>[12b-12d,13]</sup> We have shown that molecular design can be used to reduce molecular mobility of a lamellar structure, which will aid in the design of functional photoelectric materials with morphological control of lamellar structures. Further research is currently underway.

# **Experimental Section**

**General:** A series of *trans*-bis[2-(N-alkylamino)troponato- $\kappa N, \kappa O$ ]palladium(II) complexes 1a-1e was synthesized by reaction of  $Pd(OAc)_2$  with the corresponding 2-(alkylamino)tropone<sup>[16]</sup> (2 equiv.) in the presence of N, N, N', N'-tetramethylethylenediamine in boiling toluene. Melting points were measured in a glass capillary with a Büchi B-545 melting point apparatus. Mass spectra were obtained with a JEOL JMS-DX 303 spectrometer. FTIR spectra were recorded with a Bruker EQUINOX55/S spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Varian Unity-Inova 500 spectrometer. SEM images were obtained with a KEYENCE VE-7800. DSC was carried out with a Shimadzu DSC-60 instrument. XRD analyses for single crystals were conducted with a Rigaku R-AXIS RAPID imaging plate diffractometer by using graphitemonochromated Mo- $K_{\alpha}$  radiation. Powder XRD analyses were performed with a Philips X'Pert-MPD diffractometer by using  $Cu-K_{\alpha}$ radiation.

**Compound 1a:** Orange solid (24%). M.p. 116–117 °C. IR (KBr):  $\tilde{v} = 2955, 2926, 2859, 2360, 2342, 1599, 1566, 1511, 1466, 1444, 1410, 1404, 1317, 1275, 1217, 1108, 883, 752, 725 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): <math>\delta = 0.93$  (t, J = 7.0 Hz, 6 H), 1.32–1.50 (m, 8 H), 1.69 (tt, J = 7.4, 7.4 Hz, 4 H), 3.42 (t, J = 7.4 Hz, 4 H), 6.38 (dd, J = 9.9, 8.9 Hz, 2 H, 5-H), 6.59 (d, J = 9.9, 9.9, 1.1 Hz, 2 H, 6-H), 6.94 (ddd, J = 11.9, 8.9, 1.1 Hz, 2 H, 4-H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta = 14.1, 22.5, 27.7, 29.4, 49.7, 117.1, 119.3, 121.6, 133.9, 134.5, 168.3, 181.8 ppm. HRMS (FAB<sup>+</sup>): calcd. for C<sub>24</sub>H<sub>32</sub>N<sub>2</sub>O<sub>2</sub><sup>106</sup>Pd [M]<sup>+</sup> 486.1499; found 486.1525.$ 

**Compound 1b:** Orange solid (46%). M.p. 95–96 °C. IR (KBr):  $\tilde{v} = 2919$ , 2855, 1599, 1568, 1514, 1446, 1402, 1319, 1273, 1220, 716 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 0.88$  (t, J = 7.0 Hz, 6 H), 1.21–1.41 (m, 16 H), 1.45 (tt, J = 7.4, 7.4 Hz, 4 H), 1.68 (tt, J = 7.4, 7.4 Hz, 4 H), 3.41 (t, J = 7.4 Hz, 4 H), 6.38 (dd, J = 10.4, 8.8 Hz, 2 H, 5-H), 6.59 (d, J = 10.4 Hz, 2 H, 7-H), 6.65 (d, J = 11.8 Hz, 2 H, 3-H), 6.88 (ddd, J = 10.4, 10.4, 1.1 Hz, 2 H, 6-H),



6.93 (ddd, J = 11.8, 8.8, 1.1 Hz, 2 H, 4-H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta = 14.1$ , 22.7, 27.3, 28.0, 29.3, 29.4, 31.9, 49.7, 117.1, 119.3, 121.6, 133.8, 134.4, 168.3, 181.8 ppm. HRMS (FAB<sup>+</sup>): calcd. for C<sub>30</sub>H<sub>44</sub>N<sub>2</sub>O<sub>2</sub><sup>106</sup>Pd [M]<sup>+</sup> 570.2438; found 570.2447.

**Compound 1c:** Orange solid (46%). M.p. 94–95 °C. IR (KBr):  $\tilde{v} = 2919$ , 2850, 1599, 1568, 1513, 1446, 1404, 1320, 1275, 1220, 718 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 0.88$  (t, J = 7.0 Hz, 6 H, CH<sub>3</sub>), 1.20–1.33 (m, 36 H), 1.33–1.40 (m, 4 H), 1.45 (tt, J = 7.4, 7.4 Hz, 4 H), 1.68 (tt, J = 7.4, 7.4 Hz, 4 H), 3.41 (t, J = 7.4 Hz, 4 H), 6.39 (dd, J = 10.3, 8.8 Hz, 2 H, 5-H), 6.59 (d, J = 10.4 Hz, 2 H, 7-H), 6.65 (d, J = 11.8 Hz, 2 H, 3-H), 6.87 (ddd, J = 10.3, 10.3, 1.1 Hz, 2 H, 6-H), 6.94 (ddd, J = 11.8, 8.8, 1.1 Hz, 2 H, 4-H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta = 14.1$ , 22.7, 27.3, 28.0, 29.4, 29.5, 29.61, 29.66, 29.69, 29.70, 29.71, 31.9, 49.7, 117.1, 119.3, 121.6, 133.9, 134.4, 168.3, 181.8 ppm. HRMS (FAB<sup>+</sup>): calcd. for C<sub>42</sub>H<sub>68</sub>N<sub>2</sub>O<sub>2</sub><sup>105</sup>Pd [M]<sup>+</sup> 737.4331; found 737.4331.

Compound 1d: Orange solid (39%). M.p. 99–100 °C. IR (KBr):  $\tilde{v}$  = 2919, 2850, 1599, 1513, 1468, 1445, 1405, 1320, 1221, 720 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 0.88$  (t, J = 6.7 Hz, 6 H), 1.15–1.53 (m, 52 H), 1.68 (tt, J = 7.4, 7.4 Hz, 4 H), 3.41 (t, J = 7.4 Hz, 4 H), 6.38 (dd, J = 10.3, 8.8 Hz, 2 H, 5-H), 6.59 (dd, J = 10.2, 0.8 Hz, 2 H, 7-H), 6.65 (d, J = 11.9 Hz, 2 H, 3-H), 6.87 (ddd, J = 10.2,1.1 Hz, 2 H, 6-H), 6.94 (ddd, J = 11.9, 8.8, 1.1 Hz, 2 H, 4-H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 14.1, 22.7, 27.3, 27.9, 29.4, 29.5, 29.62, 29.67, 29.70, 29.71, 31.7, 49.7, 117.1, 119.3, 121.6, 133.9, HRMS 134.4. 168.3, 181.8 ppm. (FAB<sup>+</sup>): calcd. for C<sub>46</sub>H<sub>76</sub>N<sub>2</sub>O<sub>2</sub><sup>106</sup>Pd [M]<sup>+</sup> 794.4942; found 794.4922.

**Compound 1e:** Orange solid (29%). M.p. 97–98 °C. IR (KBr):  $\tilde{v} = 2919$ , 2850, 1599, 1568, 1513, 1446, 1404, 1320, 1274, 1220, 719 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 0.88$  (t, J = 7.0 Hz, 6 H), 1.20–1.33 (m, 56 H), 1.33–1.40 (m, 4 H), 1.45 (tt, J = 7.4, 7.4 Hz, 4 H), 1.68 (tt, J = 7.4, 7.4 Hz, 4 H), 3.41 (t, J = 7.4 Hz, 4 H), 6.39 (dd, J = 10.2, 8.8 Hz, 2 H, 5-H), 6.59 (d, J = 10.2 Hz, 2 H, 7-H), 6.65 (d, J = 11.8 Hz, 2 H, 3-H), 6.87 (ddd, J = 10.2, 1.1 Hz, 2 H, 6-H), 6.94 (ddd, J = 11.8, 8.8, 1.1 Hz, 2 H, 4-H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta = 14.1$ , 22.7, 27.3, 28.0, 29.4, 29.5, 29.62, 29.66, 29.71, 31.9, 49.7, 117.1, 119.3, 121.6, 133.9, 134.4, 168.3, 181.8 ppm. HRMS (FAB<sup>+</sup>): calcd. for C<sub>50</sub>H<sub>84</sub>N<sub>2</sub>O<sub>2</sub><sup>106</sup>Pd [M]<sup>+</sup> 850.5568; found 850.5596.

X-ray Structure Determination: Crystals suitable for XRD studies were obtained by recrystallization from ethyl acetate and analyzed by using a Rigaku R-AXIS RAPID imaging plate diffractometer with graphite-monochromated Mo- $K_{\alpha}$  radiation ( $\lambda = 0.71075$  Å). The structures of 1b and 1c were solved by direct methods and refined using the full-matrix least-squares method. In the subsequent refinement, the function  $\Sigma \omega (F_0^2 - F_c^2)^2$  was minimized ( $F_0$ and  $F_{\rm c}$  are the observed and calculated structure factor amplitudes, respectively). The positions of non-hydrogen atoms were found from difference Fourier electron density maps and were refined anisotropically. All calculations were performed with the Crystal Structure crystallographic software package (Rigaku), and the illustrations were produced with ORTEP.<sup>[17]</sup> Details of the structure determinations are given in Table 1, Figure 1 and Figure 2. CCDC-947886 (for 1b) and -947887 (for 1c) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

Supporting Information (see footnote on the first page of this article): <sup>1</sup>H and <sup>13</sup>C NMR spectra of **1a–1e** and DSC thermogram of **1b**.

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