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Efficient Air-Stable Organometallic Low-Molecular-Mass Gelators for Ionic Liquids: Synthesis, Aggregation and Application of Pyridine-Bridged Bis(benzimidazolylidene)–Palladium Complexes

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Dedicated to Professor Li-Xin Dai on the occasion of his 85th birthday

Abstract: Novel pincer-type, pyridine-bridged bis(benzimidazolylidene)–palladium complexes **5–7** were synthesised from cheap commercial precursors under microwave assistance. Although simple in structure, carbene complexes **5a,b** are efficient low-molecular-mass metallogelators. They gelate not only a broad variety of protic and aprotic organic solvents, but also different types of customary ionic liquids (such as imidazolium, pyridinium, pyrazolidinium, piperidinium and ammonium salts) at concentrations as low as 0.5 mg mL⁻¹. The morphologies of the resulting 3D gel networks composed from long and thin fibres were studied by TEM and

light microscopy for a selection of organic and ionic liquids. The achiral gelators are able to induce the formation of helical fibres. The thermal stability of the gel samples increases with the gelator concentration as demonstrated by thermoreversible DSC studies. Temperature-dependent NMR and X-ray diffraction studies, as well as comparisons with pincer complex analogues bearing shorter alkyl chains, suggest

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that the 3D networks responsible for gelation are based on non-covalent interactions, such as π -stacking, van der Waals interactions, and hydrogen and metal–metal bonding. Ionic liquids and gels obtained from them and **5a,b** display comparable high conductivities, which characterises pyridine-bridged bis(benzimidazolylidene)–palladium pincer complexes as air-stable metallogelators that efficiently immobilise ionic liquids in low gelator concentration indicating—beyond catalysis—their potential applications in electrochemical devices.

Introduction

Since the first stable N-heterocyclic carbene (NHC) complex was reported in 1991,^[1] a large number of NHC organo-

metallic complexes were synthesised and successfully applied as homogenous catalysts in C–C and C–N bond formation and olefin metathesis.^[2] The unique higher stability of NHC pincer complexes towards oxygen, moisture and heat makes them attractive not only as catalysts under aerobic conditions, but also as organometallics in material sciences.^[3] In this respect, however, examples demonstrating their application—especially towards soft matter^[4]—are almost neglected.

Currently, the development of simply structured molecules to immobilise fluids to form nano-scaled soft materials in a bottom-up approach is an exciting research frontier. In spite of a rapidly increasing number of reports in this field, a rational correlation of molecular structure and gelation ability in a given solvent still remains a major challenge. Due to their physical properties these low-molecular-mass-gelators (LMMGs)^[5,6] represent a particular type of soft matter^[7] and as such are attractive targets for various types of potential applications. For example, ionic liquids (ILs)

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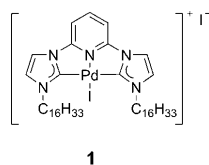
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have received considerable attention due to their high ionic conductivity and wide electrochemical window combined with high thermal and chemical stability, inflammability, extremely low volatility and a wide liquid range, which makes them attractive for application in synthesis,^[8a] material sciences^[8b] and commercial processes^[8c] such as dye-sensitised solar cells,^[9] Li-ion batteries,^[10,11] electrochemical actuators,^[12] electrochromic windows and numerical displays.^[13] Their quasi-solidification through gelation by LMMGs, especially in very low gelator concentrations, is a demanding and still difficult task which is expected to eliminate leakage problems.

Up to now, three categories of gelators—polymeric gelators,^[14] inorganic nanoparticles^[15] and LMMGs^[16]—are known to quasi-solidify ionic liquids; however, their application generally suffers from limitations such as high gelator concentration required for gel formation. To the best of our knowledge, no organometallic compound has been applied in this context. In view of the major role that organometallics play in synthesis, catalysis and supramolecular chemistry, it is surprising that their application to soft matter and LMMG has been widely neglected.^[17]

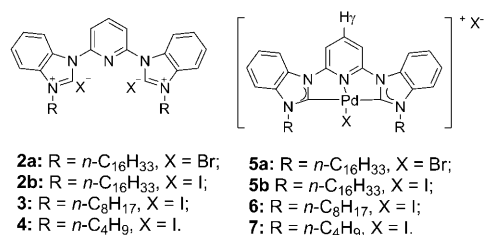
Recently, we reported the first example of a pincer bis-NHC palladium complex **1** as an efficient air-stable organometallic LMMG, which not only is able to gelate a broad variety of polar and apolar, protic and aprotic organic solvents even in concentration as



low as 0.2 wt % (2.0×10^{-3} M), but also could be applied as a supramolecular catalyst in the gel state.^[18a] Compared to imidazolylidenes, benzimidazolylidenes behave quite differently,^[19] thus, we speculated that the extended planar metal hybrid π -system and the σ -donor properties increased by benzannulation may further enhance the gelation ability and catalytic activity.^[20b] Following our recent interest in LMMGs derived from functional organometallics,^[18] we now report on a convenient synthesis of pyridine-bridged bis-(benzimidazolylidene) pincer palladium complexes starting from cheap commercially available precursors and on a comparative study of their ability to gelate a representative selection of ionic liquids.

Results and Discussion

Synthesis of pyridine-bridged bis(benzimidazolylidene) pincer palladium complexes 5–7: The amination of 2,5-difluoropyridine with two equivalents of benzimidazole to give bis(benzimidazolyl)pyridine followed by *N*-alkylation at 165 °C for 30 h with different alkyl halides in a sealed tube afforded the pyridine-bridged bis(benzimidazolium) salts **2–4** in almost quantitative yields. Subsequent cyclometalation with Pd(OAc)₂ in DMSO under microwave conditions (40 W, 160 °C, 25 min) resulted in the formation of bis(benz-



imidazolylidene) pincer palladium complexes **5–7** in 68–79% yield. Reflecting the potent gelling properties of bis-(imidazolylidene) pincer complex **1**, its benzo homologues **5a,b** are obtained as firm DMSO gels after cyclopalladation of bis(benzimidazolium) halides **2a,b** and cooling to ambient temperature after reaction.

Gelation tests with organic solvents: To test the gelation ability of carbene complexes **5–7**, a broad range of protic and aprotic solvents with different polarity and coordination ability were screened. Table 1 summarises the results of gel-

Table 1. Gelation ability of CNC pincer complexes **5** and **6** in various organic solvents.^[a]

| Entry | Solvent | 5a | 5b | 6 |
|-------|---------|--------------------|--------------------|-------------------|
| 1 | DCM | G* | G* | PG* |
| 2 | TCM | PG* ^[b] | PG* ^[b] | S |
| 3 | DCE | G | G | G |
| 4 | DMSO | G | G | S |
| 5 | DMF | G | G | S |
| 6 | DMA | G | G | S |
| 7 | THF | G* | G | P |
| 8 | ACN | I | G | G |
| 9 | AcOH | I ^[c,d] | G | G |
| 10 | MeOH | I ^[c] | I | S ^[b] |
| 11 | benzene | PG | P | WG ^[b] |
| 12 | toluene | P ^[d] | P | G |
| 13 | acetone | I ^[d] | I | I |

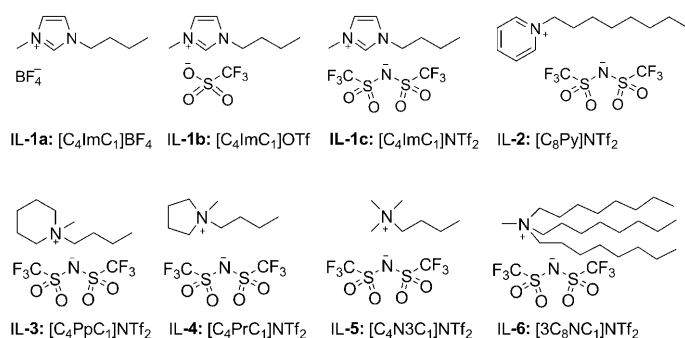
[a] Gelator concentration: 10 mg mL⁻¹; G: Gel formed at room temperature; PG: Partial gel; G* or PG*: Gel or partial gel formed by cooling to 5 °C; WG: Weak gel; S: Solution; P: Precipitate; I: Insoluble. [b] Gel formed with 20 or 30 mg mL⁻¹ at room temperature. [c] Because of low solubility, a partial gel was observed at 5 mg mL⁻¹. [d] A firm gel was formed by adding a few drops of other solvents.

ation tests of **5** and **6** with selected solvents at a concentration of 10 mg mL⁻¹. Transparent gels could be found with gelators **5a,b** in DMSO, DMF and DMA; the other gels are turbid. The colour of the gels darkens with the increasing coordination ability of the solvents as observed for the gels formed by carbene complex **1**.^[18a] When the gelator concentration was decreased to 0.5 mg mL⁻¹, stable gels still could be formed with carbene complexes **5a,b** and DMSO, which could be stored at room temperature without any visible collapse. To test the effect of the alkyl chain length on the aggregation process, carbene complexes **6** and **7** were also involved in the gelation tests. With a complex bearing shorter chain lengths (*n*-C₈H₁₇), turbid gels were formed with DCM, DCE, ACN and AcOH, and transparent gels ap-

peared with toluene and benzene at 10 mg mL^{-1} . Although a gel could not be formed with **5a** or **5b** at 10 mg mL^{-1} in MeOH, reflecting their poor solubility even at reflux condition, a yellow turbid gel was observed with gelator **6** in MeOH at 20 mg mL^{-1} (Table 1, entry 10). These results may support our assumption that—in comparison with bis(imidazolylidene) gelator **1**—extending the planar metal-hybrid π system by introducing benzimidazolylidenes into the pyridine-bridged palladium-bis(carbene) skeleton increases the gelation ability. However, no gels could be obtained with carbene complex **7** and selected organic solvents, which may be caused by less efficient van der Waals interactions between the shorter alkyl chains.

Although pyridine-bridged, bis(benzimidazolylidene)-palladium complexes are poorly soluble in acetone, no gel was obtained after cooling to room temperature. However, addition of a few drops of THF increases the solubility of **5a** and leads to gel formation (10 mg mL^{-1} , Table 1, entry 13). The same procedure was applied to the **5a**/toluene system (10 mg mL^{-1}); upon addition of a few drops of DMSO, a translucent gel was obtained (Table 1, entry 12). Compared with **5b**, carbene complex **5a** is less soluble in AcOH even at 10 mg mL^{-1} ; however, the soluble part after refluxing could form a weak gel, which makes it difficult to determine the gelator concentration. After addition of a few drops of DMSO, a homogeneous liquid phase was observed with gel **5a**/AcOH (10 mg mL^{-1}) at reflux conditions in a sealed vial forming a firm gel after cooling to room temperature.

Gelation tests with ionic liquids: As shown in Table 2, pyridine-bridged carbene complexes **5a,b** can gelate not only organic solvents, but also a variety of ionic liquids at 5 mg mL^{-1} gelator concentration. Typical types of ionic liquids, such as imidazolium salts (**IL-1a–c**), pyridinium salt



(**IL-2**), piperidinium salt (**IL-3**), pyrazolidinium salt (**IL-4**) and ammonium salts (**IL-5** and **IL-6**) have been involved in this test (Table 2).

Except **IL-2** which was synthesised according to a literature protocol,^[21] all other ionic liquids are commercially available. At room temperature, carbene complexes **5a,b** are insoluble in all selected ionic liquids. Upon heating to around $165\text{--}185^\circ\text{C}$ in a sealed vial with shaking, the resulting clear liquids form gels after cooling to room tempera-

Table 2. Gelation ability of CNC pincer complexes **5a,b** in selected ionic liquids.^[a]

| Entry | Ionic liquid | 5a | | 5b | |
|-------|---|-----------|---|-------------------|---|
| | | phase | $T_{\text{gH}} [^\circ\text{C}]^{\text{[b]}}$ | phase | $T_{\text{gH}} [^\circ\text{C}]^{\text{[b]}}$ |
| 1 | IL-1a : $[\text{C}_4\text{ImC}_1]\text{BF}_4$ | WG | 64 | WG ^[c] | — ^[d] |
| 2 | IL-1b : $[\text{C}_4\text{ImC}_1]\text{OTf}$ | WG | 66 | WG | 82 |
| 3 | IL-1c : $[\text{C}_4\text{ImC}_1]\text{NTf}_2$ | G | 87 | WG | 90 |
| 4 | IL-2 : $[\text{C}_8\text{Py}]\text{NTf}_2$ | G | 98 | G | 99 |
| 5 | IL-3 : $[\text{C}_4\text{PpC}_1]\text{NTf}_2$ | G | 96 | G | 89 |
| 6 | IL-4 : $[\text{C}_4\text{PrC}_1]\text{NTf}_2$ | G | 83 | G | 90 |
| 7 | IL-5 : $[\text{C}_4\text{N}3\text{C}_1]\text{NTf}_2$ | G | 72 | G | 80 |
| 8 | IL-6 : $[\text{3C}_8\text{NC}_1]\text{NTf}_2$ | G | 73 | WG | 76 |

[a] Gelator concentration: 5 mg mL^{-1} ; G: Gel formed at room temperature; WG: Weak gel formed at room temperature. [b] Determined by DSC. [c] Not be dissolved completely upon heating. [d] Not detected.

ture. Compared with **5a**, carbene complex **5b** is less soluble in ionic liquids based on imidazolium salts. Especially, even at a low gelator concentration of 5 mg mL^{-1} , compound **5b** cannot be dissolved completely in **IL-1a** upon heating; however, the resulting soluble part is able to form a weak gel (Table 2, entry 1). Weak gels were also observed with most imidazolium salts (**IL-1a–c**) for metallogelators **5a,b** (Table 2, entries 1–3). The weak gels obtained from **IL-1a,b** collapsed after 4–6 days at room temperature; however, that obtained from **IL-1c** (with NTf_2^- as counterion) is quite stable for several months. Therefore, we focused on selected ionic liquids containing NTf_2^- , with which firm gels were obtained with carbene complexes **5a,b** (Table 2, entries 4–8). The solubility of carbene complexes **5a,b** in most other ionic liquids under heating conditions is quite good: at 50 mg mL^{-1} metallogelators **5a,b** easily dissolve in **IL-6**, but still efficiently gelate a selection of ionic liquids even at very low gelator concentrations. For example, the lowest gelator concentration required to solidify **IL-5** by **5a,b** is 0.5 mg mL^{-1} after cooling to room temperature.

Transmission electron microscopy: The morphology of xerogels obtained from different organic solvents (after evaporation of the solvent) was investigated by transmission electron microscopy (TEM). Compared with gels formed with bis(imidazolylidene) complex **1**, slender gel fibre networks, which are composed of long (several μm) and thin (10–100 nm wide) fibres, were observed in the gels formed with bis(benzimidazolylidene) complexes **5a,b** in most selected solvents. In most cases, gels formed with **5a,b** reveal a twisted helical ribbon morphology at the microscopic level, which is quite rarely observed in gel networks formed from achiral gelators.^[18a] The dimensions of the individual fibres vary with the gelator and solvents used. Selected TEM images of gels with helical morphologies (*P* and *M*) formed by carbene complexes **5a,b** are presented in Figure 1. Helical fibres that are about 100 nm wide and 500–600 nm in pitch were observed with gel **5a**/DCE (Figure 1a); thinner (ca. 70 nm wide) and longer (up to 100 μm long) fibres with a pitch of about 500 nm were encountered in the gel **5b**/DCE (Figure 1c). More helical fibres with a pitch of approximately 250 nm and 50 nm in width appeared in the TEM

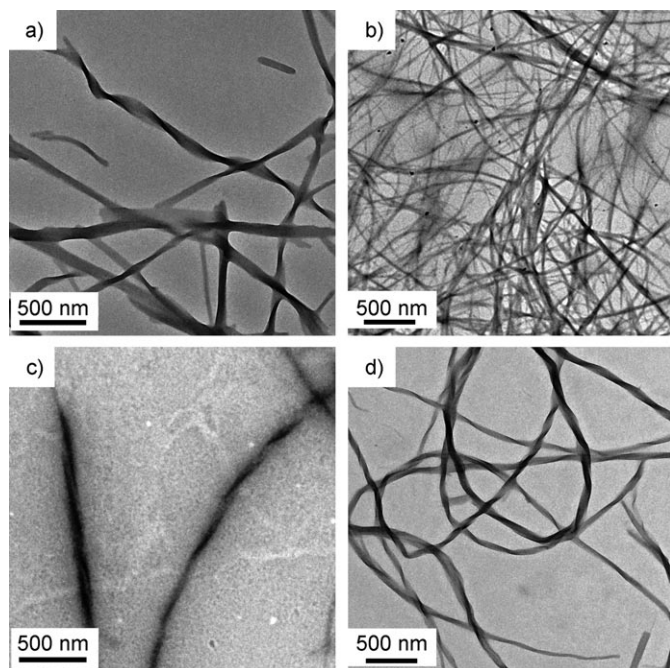


Figure 1. Selected TEM images of gels formed by CNC pincer complexes **5a,b** (10 mg mL^{-1}): a) Gel **5a**/DCE; b) gel **5a**/DMA; c) gel **5b**/DCE; and d) gel **5b**/AcOH.

image of xerogel **5b**/AcOH (Figure 1d). As shown in Figure 1b, a denser gel network with thinner (around 10 nm wide) and long helical fibres was observed with gel **5a**/DMA; a similar morphology was found with gel **5a**/DMF.^[22] Very dense gel networks result from gels **5a,b**/DMSO, **5b**/DMF and **5b**/DMA. More straight and broad fibres were obtained from gels **5a,b** with ACN, DCM, TCM and THF,^[22] which may suggest gels formed by a parallel columnar self-assembly.

TEM was also applied to investigate the morphologies of gels obtained from mixtures of solvents. Ribbon-type fibres, approximately 150 nm wide and several μm long,^[22] were observed in the dense network of gel **5a**/(toluene+DMSO). In contrast, the morphologies of gels obtained from two other mixtures of solvents are quite different. Bold fibres (0.5–1 μm wide) were present in the xerogel network of **5a**/(AcOH+DMSO) (Figure 2a), at the end of which small hair-like twisted fibres (ca. 10 nm wide) emerge. A Chinese chrysanthemum-like xerogel network (Figure 2b) appears in the morphology of gel **5a**/(acetone+THF). The diameter of the flower is around 5–10 μm . The fibres emerging from the core of flower are approximately 100 nm wide.

Dark-field optical microscopy: (Xero)gels of ionic liquids suf-

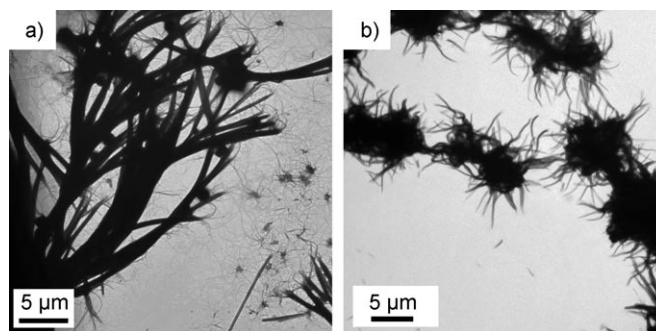


Figure 2. TEM images of gels formed by CNC pincer complexes **5a** in solvents containing a few drops of cosolvent (10 mg mL^{-1}): a) Gel **5a**/(AcOH+DMSO) and b) gel **5a**/(acetone+THF).

ferred from decomposition when irradiated with the electron beam, which hampered the recording of satisfactory TEM images. Therefore, dark-field optical microscopy was involved to get a direct visual insight into the gel morphologies obtained from gelators **5a,b** and various ionic liquids. Selected images are shown in Figure 3. In most cases, straight and long cotton-like fibre (10–25 μm long and ca. 500 nm wide) gel networks were observed under the microscope. In the gel morphologies of **5a**/IL-1b, **5b**/IL-1c and **5a,b**/IL-5, shining rod-like particles were observed within these straight and long fibre networks,^[22] which may reveal that a lamellar assembly is also responsible for the gel formation with gelator **5a,b** and ionic liquids. Short and twisted wool-like fibres were found with the gels **5a**/IL-1c and **5a**/IL-2.^[22] As observed in the xerogel networks obtained from gelators **5a,b** and some organic solvents, helical-like fibres (approximately 100 μm long and 0.5–0.8 μm wide, with a pitch of 20 μm) could be found in the gel **5a**/IL-3 (Figure 3a). This type of helical fibres may also exist in the other gel samples such as **5b**/IL-2 (Figure 3b); the low resolution of light microscopy in comparison to TEM hampers the observation of more detailed information.

Thermal stability of the gels: The gel–sol phase-transition temperatures (T_g) of gels in selected solvents were determined by differential scanning calorimetry (DSC).^[5,23] The

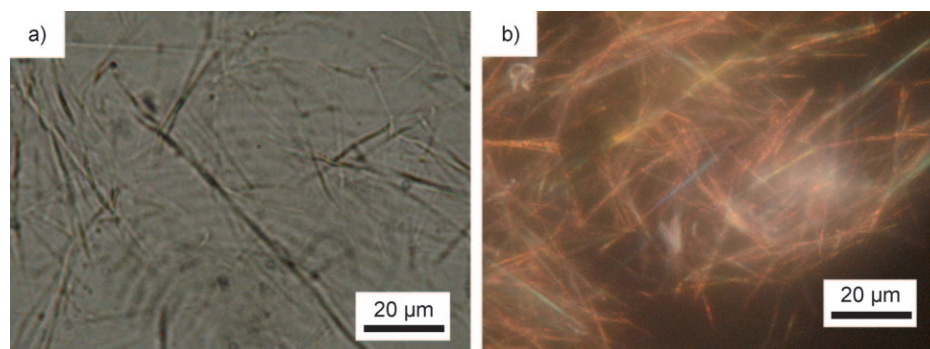


Figure 3. Selected dark-field optical microscopic images of gels formed by CNC pincer complexes **5a,b** (5 mg mL^{-1}) with ionic liquids: a) Gel **5a**/IL-3; and b) gel **5b**/IL-2.

DSC thermograms revealed well-defined thermo-reversible gel–sol transitions with accurate T_g and enthalpy parameters, which indicate that the 3D networks responsible for gelation are built up by non-covalent interactions, such as π -stacking, hydrogen bonding and van der Waals interactions. In all tested gels, the gel–sol phase-transition temperatures ($T_{g/H}$) were found to be approximately 15 °C higher than those observed for the sol–gel conversion ($T_{g/C}$), a hysteresis behaviour which is characteristic of LMMGs.^[18a,24] Although bis-(benzimidazolylidene)–palladium complexes **5a,b** quite efficiently gelate DMSO at concentrations even as low as 0.5 mgmL⁻¹ (0.05 wt %, w/v), these conditions are hard to realise. Therefore, a series of **5a,b**/DMSO gels with concentrations varying from 1 to 30 mgmL⁻¹ were studied by DSC and the “dropping ball method”^[24] in order to examine the effect of concentration of the gelator on the sol–gel transition temperatures. When the gelator concentration is lower than 2 mgmL⁻¹, it is difficult to determine $T_{g/H}$ by DSC, because of the low melting point of DMSO (292 K) and the difficulty to transfer the low concentration gel samples into the aluminium crucibles. Thus, we applied the dropping ball method in the $T_{g/H}$ tests. Figure 4 shows that $T_{g/H}$ and $T_{g/C}$ increase with increasing concentration of gelators **5a,b** in DMSO, which demonstrates that the thermal stability of the gels formed with organic solvents increases with increasing gelator concentration.

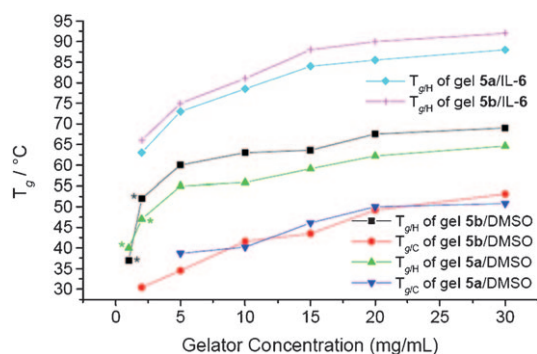


Figure 4. Sol–gel transition temperatures as a function of gelator concentration: $T_{g/H}$ and $T_{g/C}$ for gels **5a,b**/DMSO (* means that $T_{g/H}$ was measured by the “dropping ball method”) and $T_{g/H}$ for gels **5a,b**/IL-6.

The $T_{g/H}$ of gels obtained with all ionic liquids studied at 5 mgmL⁻¹ gelator concentration were determined by DSC and corroborated by the “dropping ball method”, the results are summarised in Table 2. Compared with the $T_{g/H}$ (at 10 mgmL⁻¹) for gels prepared with organic solvents, the $T_{g/H}$ of gels obtained from selected ionic liquids (at 5 mgmL⁻¹) are higher and generally above 65 °C (Table 2). With ionic liquids, the $T_{g/H}$ also increase with the gelator concentration which confirms a similar thermal behaviour as previously observed for organic solvents. For example, an increase of the gelator concentration of gel **5a**/IL-6 from 2 to 30 mgmL⁻¹ induced an increase of the gel–sol phase-transition temperatures (T_g) from 63 to 88 °C as shown in

Figure 4. Similar results were observed with gel **5b**/IL-6 (from 66 to 92 °C).

Temperature-dependent ¹H NMR study: Similar to metallo-gelator **1**, the efficiency observed for carbene complexes **5a,b** and even **6** gelating a broad variety of organic solvents and ionic liquids may be caused by the extended planar metal-chelating pincer ring, which allows for aggregation by intermolecular π -stacking, possibly enhanced by van der Waals interactions between the alkyl chains and by metal–metal interactions. Therefore, temperature-dependent ¹H NMR spectroscopic studies of gel **5a,b**/[D₆]DMSO (at 5 mgmL⁻¹ and 10 mgmL⁻¹) were applied to probe the role of the metal-hybrid aromatic rings during the gelation process. Almost no clear proton signals were detected at room temperature for gel sample **5b**/[D₆]DMSO (5 mgmL⁻¹) and broad signals appeared even at 308 K, which indicates an extensive aggregation in the gel state.^[22] Upon warming to 348 K by 10 K steps, the broad signals observed for the hetero-aromatic and the *N*-CH₂ hydrogen atoms steadily sharpen and are shifted downfield: The signals of the γ proton of the pyridine ring and *N*-CH₂ are shifted from $\delta = 7.82$ and 4.32 to 8.02 and 4.52 ppm, respectively, ($\Delta\delta$ is 0.2 ppm) over the temperature range of 40 K (308–348 K). A similar phenomenon was observed with gel **5a**/[D₆]DMSO (5 mgmL⁻¹). When the concentration was increased to 10 mgmL⁻¹, broad signals were observed even at 328 K, which also confirmed the results derived from the increase of T_g with the gelator concentration. Upon warming from 328 K to 348 K, the proton signals steadily sharpen and are shifted downfield with a $\Delta\delta$ of 0.16 ppm for the γ proton.^[22] This effect is thermo-reversible and reflects strong aromatic π – π interactions between the gelator molecules.

X-ray structure of complex 7: Although carbene complex **7** is not able to gelate selected liquids, its crystal structure may help to further understand the self-assembling process of bis(carbene) complexes **5–7**. Exposure of a solution of **7** in CHCl₃ to vapor of MeOH induced the formation of orange needle-shaped single crystals of the composition of 7·0.81 CHCl₃. Its structure is depicted in Figure 5, and crystallographic details are provided in the Supporting Information. The terminal methyl groups of the butyl chains and the guest molecules (CHCl₃) are partially disordered. Unlike the structures reported for CNC pincer palladium carbene complexes,^[18a,26,27] the structure is very symmetric (Figure 5a): Two I⁻ ions are located vertically above and below the plane of the metal-chelating pincer ring with equal distances to the metal (2.79 Å). The extended metal-hybrid π system slightly deviates from planarity, the benzene rings are slightly out of the plane (ca. $\pm 3.2^\circ$) that is defined by palladium, the pyridine and imidazole rings. Strong π – π interactions (ca. 3.3 Å, Figure 5b) are observed between the extended palladium-hybrid planes. Unlike the metal–metal bonding found in the crystal of the butyl analogue of carbene complex **1**,^[18a] there is no evident Pd...Pd interaction, which may reflect the steric hindrance by the counter ion

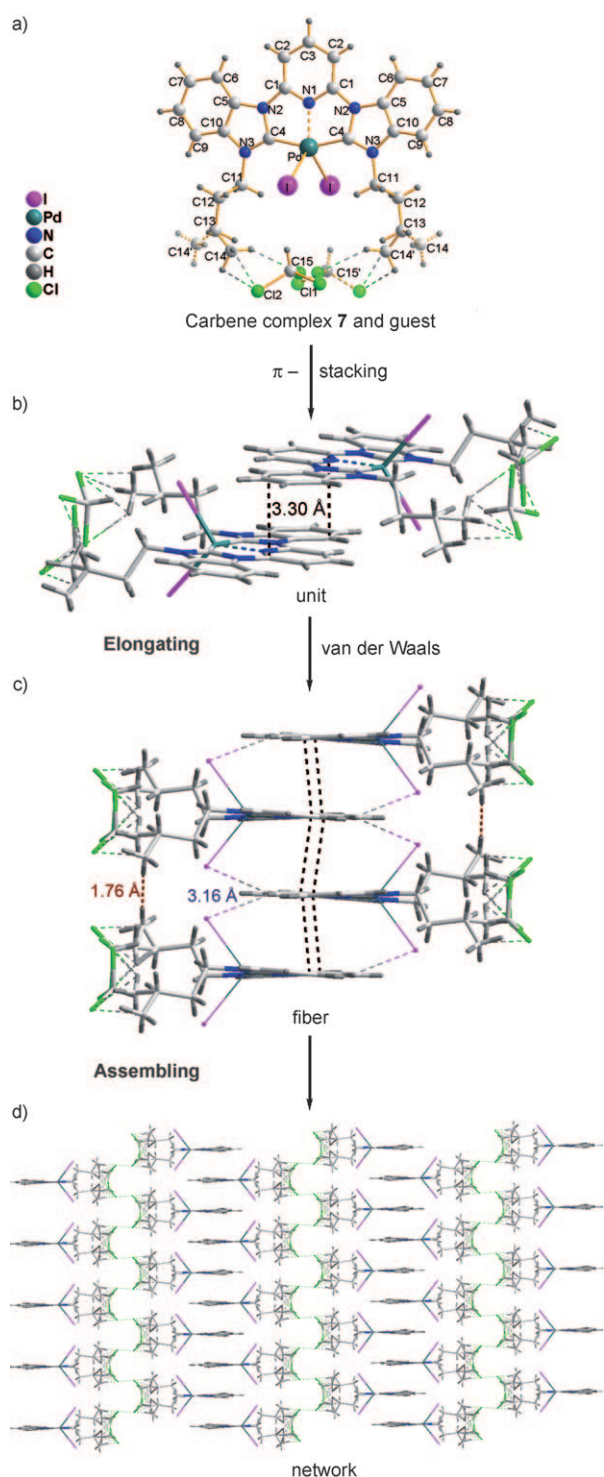


Figure 5. a) Molecular structure of **7**·0.81 CHCl₃ in the crystal; b) π interactions between extended metal hybrid π rings of two adjacent molecules to form units; c) van der Waals interactions between the alkyl chains resulting in fibres; and d) side view showing part of a truncated 2×2 array of unit cells.

(I⁻) in the solid state. The π interactions between the molecules are responsible for the formation of aggregation units, which are assembled to fibres through strong intermolecular

van der Waals interactions with the shortest distance of 1.76 Å between the hydrogen atoms of terminal butyl chains belonging to two adjacent molecules (Figure 5c). Some weak intermolecular interactions are observed within the units; for example, the distance between I⁻ and the β hydrogen atom of the pyridine ring of the adjacent molecule is 3.16 Å. As shown in Figure 5a, the solvate guests have very strong hydrogen-bonding interactions with the butyl chains, which may reveal how the gelator cages the solvent during the gelation. The shortest H...Cl distance is 2.18 Å, the others vary from 2.42 to 2.69 Å. By this means, two elongating fibres may assemble through hydrogen-bonding interactions with solvent guests to form a parallel columnar packing pattern in the crystal network (Figure 5d).

Although there are no evident metal–metal interactions observed in the crystal structure (solid state) of carbene complex **7** as a consequence of the steric hindrance by the counterions, we believe that Pd...Pd interactions still play a key role during the aggregation process to form a gel for the following reasons. Bis(benzimidazolium) salts **2a,b** and **3** efficiently gelate a variety of organic solvents (especially a broad variety of alcohols) even at the gelator concentration of 5 mg mL⁻¹,^[20a] but, unlike gelators **5a,b**, are unable to gelate DMSO, DCE and other solvents. In addition, the structure and dimensions of the gel network of **5a,b**/DMSO have been studied by X-ray diffraction (Figure 6).^[5,28] Similar X-ray diffraction patterns could be observed with gels **1**/DMSO and **5b**/DMSO with the only difference that the intensities of the reflections are less prominent in the latter (Figure 6). The broad reflection at $q = 2.1 \text{ nm}^{-1}$ and the sharp reflection at $q = 4.2 \text{ nm}^{-1}$ may suggest that the structure in the gel state resembles that of the crystal structure shown in Figure 5d. The alkyl chains are lined up with a distance of approximately 1.5 nm ($= 2\pi/4.2$) in real space (sharp reflection), whereas the Pd, the pyridine and imidazole rings are stacked with a corresponding distance of 3 nm (broad reflection), but in a less pronounced order, maybe due to steric reasons. Differently, the gel **5a**/DMSO exhibits a clear lamellar arrangement (reflections at $q = 1.72, 3.53$ and 5.2 nm^{-1}) with a corresponding distance of 3.6 nm in real space. This reflects the significantly higher order of the stacked layers of the complex with long alkyl chains and bromide counterions instead of iodide. An additional feature, which is common to all three gels, is the peak at $q = 16 \text{ nm}^{-1}$, which corresponds to a distance of 3.8 Å in real space and is attributed to a π stacking and Pd...Pd interactions. This distance is slightly larger in the gel state than in the crystal. The intensity in the small-angle X-ray scattering range towards low q values (Figure 5a) shows an increase that may be caused by the arrangement of the basic units in the formation of elongated fibres. The typical diameter of a fibre is about 9 nm (which is similar to the fibre dimension, ca. 10 nm wide, observed for TEM with gels **5a,b**/DMSO), which is derived from the shoulder in the intensities towards low q -values.

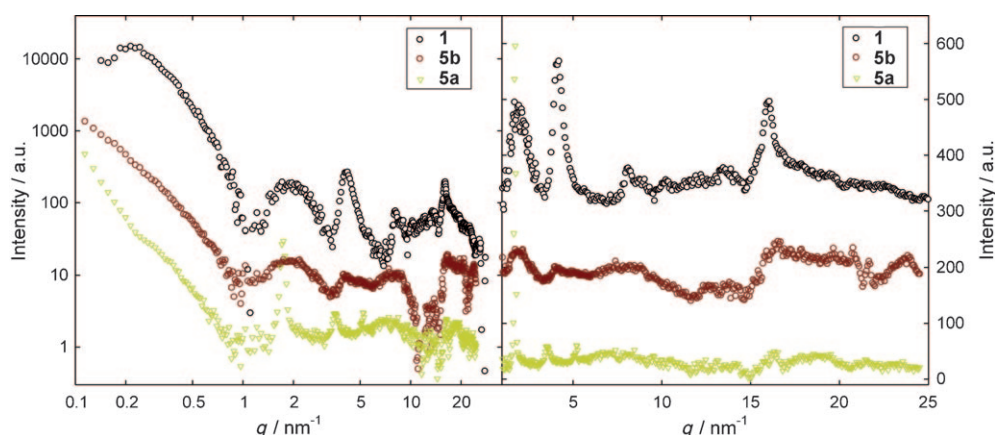


Figure 6. X-ray diffraction patterns of gels **1**/DMSO and **5a,b**/DMSO (3 wt %) after subtraction of the solvent-based background: left: logarithmic scale and right: linear scale; the curves are vertically shifted for clarity.

Conductivity of the gels formed by ionic liquids: Ionic liquids are a new type of electrolytes with a high conductivity for ions. Currently, solid electrolytes, which are electrically conductive solids with ionic carriers, attract much attention because of their wide potential applications in the field of electrochemical devices. Therefore, the immobilisation of ionic liquids while maintaining high conductivity to produce solid electrolytes is a very important issue. Since metallo-gelators **5a,b** quite efficiently gelate a variety of ionic liquids even at very low gelator concentrations, they provide a convenient method to obtain quasi-solid electrolytes. The conductivity (σ_s) of different gels (5 mgmL⁻¹) formed by gelators **5a,b** and eight ionic liquids are listed in Table 3. Gen-

Table 3. Ionic conductivities of selected pure ionic liquids and corresponding gels formed from CNC pincer complexes **5a,b**.^[a]

| IL | σ_0 [S cm ⁻¹] | gel 5a /IL σ_s [S cm ⁻¹] | σ_s/σ_0 | gel 5b /IL σ_s' [S cm ⁻¹] | σ_s'/σ_0 |
|-------|----------------------------------|---|---------------------|--|----------------------|
| IL-1a | 3.98×10^{-3} | 3.78×10^{-3} | 0.95 | $3.82 \times 10^{-3[b]}$ | 0.96 ^[b] |
| IL-1b | 2.90×10^{-3} | 2.89×10^{-3} | 1.00 | 2.91×10^{-3} | 1.00 |
| IL-1c | 4.40×10^{-3} | 4.29×10^{-3} | 0.98 | 4.28×10^{-3} | 0.98 |
| IL-2 | 1.18×10^{-3} | 1.12×10^{-3} | 0.95 | 1.13×10^{-3} | 0.95 |
| IL-3 | 1.58×10^{-3} | 1.48×10^{-3} | 0.94 | 1.55×10^{-3} | 0.98 |
| IL-4 | 2.88×10^{-3} | 2.86×10^{-3} | 0.99 | 2.78×10^{-3} | 0.97 |
| IL-5 | 2.20×10^{-3} | 2.20×10^{-3} | 1.00 | 2.29×10^{-3} | 1.04 |
| IL-6 | 6.07×10^{-5} | 6.15×10^{-5} | 1.01 | 6.22×10^{-5} | 1.02 |

[a] Conductivities of pure ionic liquids and gels **5a,b**/IL were measured at 25 °C. [b] **5b** cannot be dissolved completely upon heating.

erally, a conductivity exceeding 1 mS cm⁻¹, which is significantly higher than that of Li-conducting solid polymer electrolytes applied in various devices,^[10] is appealing for a solid electrolyte. This property is realised for all gel samples studied with the exception of those formed with IL-6 (Table 3, entries 1–7). For comparison, the ionic conductivities (σ_0) of pure ionic liquids were also measured. Unlike the evident difference in conductivity between the pure ionic liquids and the ionic liquid gels prepared from reported organic LMMGs,^[16] the ionic conductivities of the gel samples are

very close to those of the pure ionic liquids. In some case, σ_s is even higher than σ_0 (Table 3, IL-5 and IL-6), which may fulfill the requirements of quasi-solidification of ionic liquids to produce solid electrolytes. For 30 mg mL⁻¹, the conductivity (σ_{30}) of gel **5a**/IL-6 at room temperature is 6.39×10^{-5} S cm⁻¹ revealing that the conductivity further increases with gelator concentration. This phenomenon is in contrast with results reported in the literature stating a decrease of the ionic conductivity with the organic gelator concentration,^[16a] but may be rationalised in terms of the ionic property of pyridine-bridged palladium–carbene complexes **5a,b**. The conductivities of iodide gels (**5b**) are slightly higher than those of bromide gels (**5a**), which may reflect the better leaving group property of I⁻ compared to Br⁻ in the complexes (Table 3).

The temperature dependence of the ionic conductivity was studied with a series of 5 mg mL⁻¹ gels obtained from **5a,b** and selected various ionic liquids. Figure 7 shows the plots of ionic conductivities of the quasi-solidified ionic liquids against temperature (25–100 °C). As expected for the pure ionic liquids, the ionic conductivities of the metallo-gels also steadily increased upon heating. For some pairs of gels, a conductivity cross-over is observed. For example, the con-

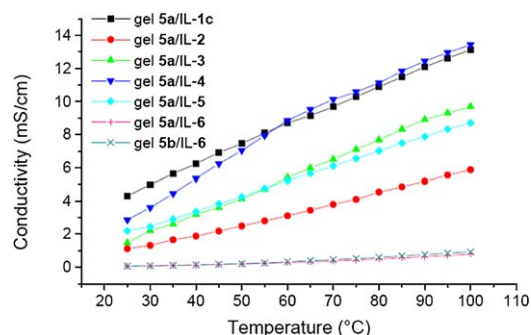


Figure 7. Temperature-dependent ionic conductivities of quasi-solidified ionic liquids formed by CNC pincer complexes **5a,b** (gelator concentration: 5 mg mL⁻¹).

ductivities (σ_s) of gels **5a/IL-1c** and **6a/IL-4** are 4.29×10^{-3} and $2.86 \times 10^{-3} \text{ Scm}^{-1}$ at 25°C , (Table 3, **IL-1c** and **6**), and they increase to 13.13×10^{-3} and $13.43 \times 10^{-3} \text{ Scm}^{-1}$ at 100°C . Similar phenomena were also observed with gels **5a/IL-3** and **5a/IL-5** (Figure 7). As shown in Table 3, the conductivity (σ_s) of gels **5b/IL-6** is slightly higher than that of **5a/IL-6**, and this tendency is kept upon heating, which indicates that the counterion affects the gelator property and the conductivity of the quasi-solids. The gel-sol transition temperature ($T_{g/H}$) of 5 mg mL^{-1} samples prepared from **5a,b** and all selected ionic liquids are in the range of $65\text{--}100^\circ\text{C}$ (Table 2), the σ_s versus T plots are quite linear indicating that the activation energies for the phase transitions are similar and that gels prepared from gelators **5a,b** and ionic liquids maintain the isotropic properties on a microscopic scale, although ionic liquids are immobilised to form a 3D network on a macroscopic scale. This property may offer potential applications of pyridine-bridged bis-(benzimidazolylidene) pincer carbene complexes in electrochemical devices.

Conclusions

In conclusion, a novel pincer-type of pyridine-bridged bis-(benzimidazolylidene)-palladium complexes was synthesised from cheap commercially available precursors under microwave assistance and successfully applied as efficient organometallic gelators for a variety of protic and aprotic organic solvents as well as ionic liquids effective in concentrations as low as 0.5 mg mL^{-1} . π -Stacking of the extended planar metal-hybrid (hetero)arene moieties, van der Waals interactions between the alkyl chains, and metal-metal interactions may be responsible for the aggregation as supported by temperature-dependent NMR spectroscopy and X-ray diffraction studies. Since pure ionic liquids and corresponding gels prepared from them and **5a,b** show comparable high conductivities, pyridine-bridged bis(benzimidazolylidene)-palladium complexes represent the first examples of air-stable metallogelators which efficiently immobilise ionic liquids in very low gelator concentration, indicating potential applications—beyond catalysis—also in electrochemical devices.

Experimental Section

All commercial reagents and solvents were used directly as purchased without further purification. **IL-2** was synthesised by a literature method.^[21] The other ionic liquids were bought from Fluka and Roth. All reactions were carried out in air unless otherwise noted. ^1H and ^{13}C NMR spectra were recorded on Bruker 500 DRX/400 DPX/300 DPX spectrometers. MALDI-TOF mass spectra were recorded on a Bruker Daltonics Announces Autoflex TOF/TOF mass spectrometer using DCTB as matrix; ESI-MS spectra were recorded on a micrOTOF-Q Bruker Daltonik instrument. Conductivities of gel samples and pure ionic liquids were measured by a Mettler Toledo FiveGo (FG3) conductometer within a temperature range of $0\text{--}100^\circ\text{C}$. Before every testing, the conductometer was calibrated with standard solutions ($84 \mu\text{Scm}^{-1}$,

$1413 \mu\text{Scm}^{-1}$ and 12.88 mScm^{-1}). A CEM Discover microwave instrument was applied for the palladation.

The synthesis of bis(benzimidazolium) salts (**2-4**)^[20], crystallographic data of carbene complex **7**, details of gel preparation and characterisation, as well as additional TEM and dark-field microscopic images are provided in the Supporting Information.

Synthesis of bis(benzimidazol-2-ylidene)-palladium complexes (5-7): A solution of pyridine-bridged benzimidazolium salt (1.0 mmol) and Pd(OAc)₂ (0.224 g, 1.0 mmol) was stirred in DMSO (8 mL) for 1 h at room temperature under vacuum. After refilling the flask with argon, the mixture was exposed to microwave radiation with stirring in the open vessel model for 25 min at 160°C (at 40 W with a CEM Discover instrument). Cold Et₂O was added (200 mL) and the precipitate was purified three times by dissolving in hot CHCl₃ and precipitating with cold Et₂O, affording a yellowish solid.

Carbene complex 5a: Yield: 76%; ^1H NMR ([D₆]DMSO, 500 MHz, 348 K): δ = 7.95 (t, J = 8.5 Hz, 1 H), 7.81 (d, J = 8.5 Hz, 2 H), 7.76 (d, J = 8.5 Hz, 2 H), 7.39 (d, J = 7.5 Hz, 2 H), 7.02–7.10 (m, 4H), 4.37 (t, J = 7.8 Hz, 4H), 1.30 (quintet, J = 7.5 Hz, 4H), 0.88 (quintet, J = 7.5 Hz, 4H), 0.74 (m, 4H), 0.61–0.70 (m, 44H) 0.24 ppm (t, J = 7.0 Hz, 6H); ^{13}C NMR ([D₆]DMSO, 125 MHz, 338 K): δ = 175.85, 151.52, 147.68, 134.41, 130.31, 127.79, 127.10, 114.39, 114.00, 110.59, 48.55, 32.07, 30.66, 29.81, 29.67, 29.63, 29.56, 29.44, 29.40, 26.59, 22.82, 14.59 ppm; HR-MS (MALDI, DCTB); m/z calcd: 946.4401; found: 946.4620 [M-Br]⁺; elemental analysis calcd (%) for C₅₁H₇₇Br₂N₅Pd·2H₂O (1059.3792): C 57.65, H 7.68, N 6.59; found: C 57.78, H 7.22, N 6.54.

Carbene complex 5b: Yield: 79%; ^1H NMR ([D₆]DMSO, 500 MHz, 348 K): δ = 8.02 (t, J = 8.2 Hz, 1 H), 7.87 (d, J = 7.8 Hz, 2 H), 7.83 (d, J = 8.3 Hz, 2 H), 7.44 (d, J = 8.0 Hz, 2 H), 7.05–7.15 (m, 4H), 4.52 (t, J = 8.0 Hz, 4H), 1.33 (quintet, J = 7.5 Hz, 4H), 0.92 (quintet, J = 7.5 Hz, 4H), 0.77 (m, 4H), 0.43–0.54 (m, 44H) 0.24 ppm (t, J = 7.0 Hz, 6H); ^{13}C NMR ([D₆]DMSO, 125 MHz, 338 K): δ = 176.34, 151.34, 147.50, 134.20, 130.43, 127.84, 127.16, 114.57, 114.08, 110.61, 61.28, 50.15, 32.08, 30.85, 29.81, 29.62, 29.56, 29.43, 26.33, 22.83, 14.63 ppm; HR-MS (MALDI, DCTB); m/z calcd: 992.4258; found: 992.4613 [M-I]⁺; elemental analysis calcd (%) for C₅₁H₇₇I₂N₅Pd·H₂O (1137.3409): C 53.81, H 6.99, N 6.15; found: C 53.85, H 6.93, N 6.15.

Carbene complex 6: Yield: 71%; ^1H NMR ([D₆]DMSO, 500 MHz, 338 K): δ = 7.81 (t, J = 8.0 Hz, 1 H), 7.65 (d, J = 7.5 Hz, 2 H), 7.61 (d, J = 8.3 Hz, 2 H), 7.23 (d, J = 7.5 Hz, 2 H), 6.85 (quintet, J = 7.5 Hz, 4H), 4.25 (t, J = 8.0 Hz, 4H), 1.10 (quintet, J = 7.5 Hz, 4H), 0.72 (quintet, J = 7.5 Hz, 4H), 0.56–0.60 (m, 4H), 0.43–0.54 (m, 10H) 0.10 ppm (t, J = 6.8 Hz, 6H); ^{13}C NMR ([D₆]DMSO, 125 MHz, 338 K): δ = 176.2, 151.2, 147.6, 134.1, 130.3, 127.9, 127.2, 114.5, 114.1, 110.6, 50.2, 31.9, 30.9, 29.4, 29.3, 26.4, 22.8, 14.6 ppm; HR-MS (MALDI, DCTB); m/z calcd: 768.1754; found: 768.2006 [M-I]⁺; elemental analysis calcd (%) for C₃₅H₄₅I₂N₅Pd·0.5H₂O (904.0852): C 46.45, H 5.12, N 7.74; found: C 46.46, H 5.49, N 7.48.

Carbene complex 7: Yield: 68%; ^1H NMR ([D₆]DMSO 500 MHz, 298 K): δ = 7.74 (t, J = 8.3 Hz, 1 H), 7.64 (d, J = 8.0 Hz, 2 H), 7.60 (d, J = 8.3 Hz, 2 H), 7.22 (d, J = 7.8 Hz, 2 H), 6.81–6.90 (m, 4H), 4.24 (t, J = 7.5 Hz, 4H), 0.95–1.11 (m, 4H), 0.66 (quintet, J = 7.5 Hz, 4H), 0.10 ppm (t, J = 7.3 Hz, 6H); ^{13}C NMR ([D₆]DMSO, 125 MHz, 298 K): δ = 176.08, 151.32, 147.46, 134.12, 130.35, 127.83, 127.14, 114.64, 114.13, 110.61, 61.11, 33.09, 19.94, 14.65 ppm; HR-MS (ESI); m/z calcd: 782.9547, 656.0502; found: 782.9588 [M]⁺, 656.0503 [M-I]⁺; elemental analysis calcd (%) for C₂₇H₂₉I₂N₅Pd·0.5DMSO (904.0852): C 40.48, H 3.88, N 8.13; found: C 40.63, H 3.92, N 8.14.

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