DOI: 10.1002/anie.200701980

Supramolecular Assemblies

Supramolecular Assemblies Based on Organometallic Quinonoid Linkers: A New Class of Coordination Networks

Jamal Moussa and Hani Amouri*

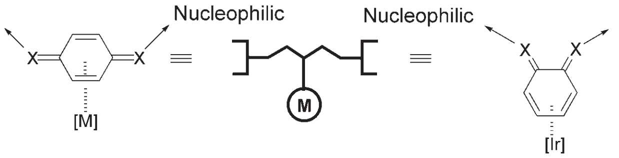
iridium · metal–metal interactions · reactive intermediates · supramolecular chemistry · thioquinones

*Self-assembly of coordination frameworks exhibiting original architectures is an active area of research. Generally, such assemblies are constructed from organic spacers and transition metals of different geometrical structures. Herein, we report a novel class of supramolecular coordination assemblies with organometallic linkers based on metalated quinonoid and thioquinonoid complexes that serve as spacers. The organometallic ligands are stable and have the general formula [Cp*M(η^4-benzoquinone)] (o- and p-benzoquinone, Cp* = C_5Me_5, M = Rh, Ir) and [Cp*Ir(η^4-thiobenzoquinone)] (o- and p-thiobenzoquinone). These units bind through both oxygen or sulfur atoms to metal ions of different coordination geometry, such as Cu^I, Ag^I, and Pt^{II}, to generate supramolecular coordination networks, with the metalated quinonoid or thioquinonoid linkers acting as backbones and the metal centers as nodes. This novel family of supramolecular assemblies exhibits short π–π and M···M interactions. These results illustrate successfully the role of the organometallic linkers to produce an impressive range of novel supramolecular architectures that hold promise for the development of functional materials.*

1. Introduction

Supramolecular assemblies constructed from their individual components through a bottom-up strategy represent an area of intense research activity.[1–7] This interest is justified, owing to the need for novel functional materials with technological applications. Such supramolecular systems possess functionality that makes them attractive for a number of potential applications, including molecular wires,[8–13] catalysts,[14] chemical sensors,[15,16] photoluminescence materials,[17] and molecular magnets.[18] To date, most of these supramolecular species self-assemble by combination of metal ions of different coordination geometries and a variety of organic bridging ligands. In only a few examples was a metalated bridging ligand used.[19–21] In contrast, we have recently found that our rhodium and iridium *p*-benzoquinone complexes [Cp*M(*p*-benzoquinone)] (M = Rh, L^{Rh}; M = Ir, L^{Ir}) are stable, easy to prepare, and adequate organometallic bridging ligands[22–25] to construct a novel family of supramolecular assemblies (Figure 1).

In fact, the activated 1,2- or 1,4-oxygen and sulfur centers in these metal quinonoid linkers are nucleophilic enough to coordinate to electrophilic metal ions that prefer different geometries, thus providing a variety of supramolecular structures (Scheme 1). Moreover, the presence of a metal



X = O, [M] = Cp*Rh **2a**, Cp*Ir **2b**
X = S, [M] = Cp*Ir **2e**

X = O, [Ir] = Cp*Ir **2c**
X = S, [Ir] = Cp*Ir **2d**

Figure 1. Organometallic linkers **2a**–**e**.

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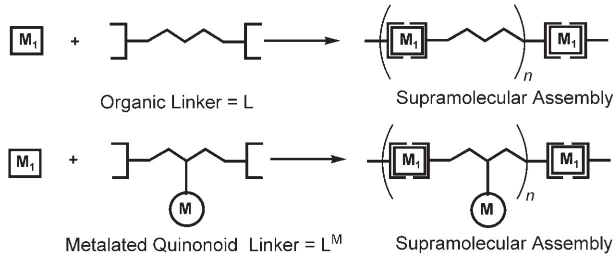
[*] J. Moussa, Dr. H. Amouri
Laboratoire de Chimie Inorganique et Matériaux Moléculaires, UMR CNRS 7071
Université Pierre et Marie Curie-Paris 6
4 place Jussieu, case 42, 75252 Paris Cedex 05 (France)
Fax: (+33) 1-4427-3841
E-mail: amouri@ccr.jussieu.fr



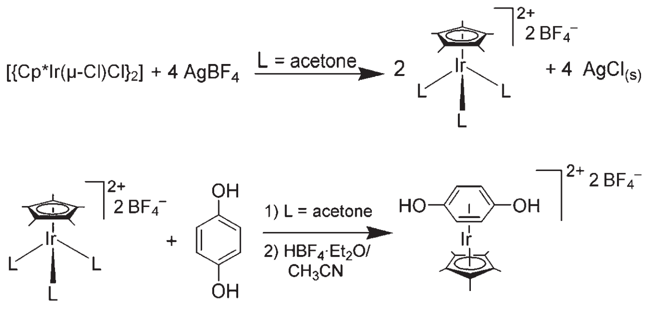
Scheme 1. Supramolecular assemblies with organic or metalated quinonoid linkers.

center within the assembling unit L^M is of high importance, as it provides an additional functionality to the coordination assembly. Most of these supramolecular species are positively charged, and hence they are potentially useful for anion sensing or templating and in photoluminescence, owing to presence of coinage metals and platinum(II) subunits. As far as we are aware, prior to our work the only known organometallic quinonoid linker was Na[$(CO)_3$Mn(*p*-benzoquinone)], which was used to prepare neutral 1D, 2D, and 3D networks.[26] However, none of these polymers featured silver cations or platinum subunits. Thus, our supramolecular assemblies differ completely in their coordination mode and their properties from those reported previously.

Herein, we report some of these supramolecular assemblies based on neutral quinonoid linkers (rhodium and iridium *p*-benzoquinone) and extend this concept to a new family of thioquinonoid linkers (iridium *o*- and *p*-dithiobenzoquinone) reported by us for the first time. We also discuss their utility in assembling coinage metal ions such as Cu^I and Ag^I as well as Pt^{II} complexes, thus providing novel, appealing architectures in which the metal ions are in close contact. Furthermore, the Pt coordination assemblies with Pt···Pt and π–π interactions exhibit strong UV/Vis absorption and luminescence.[27] This property, as well as the appealing molecular structures of our coordination polymers with organometallic linkers, reflects the variety and richness of this new field.

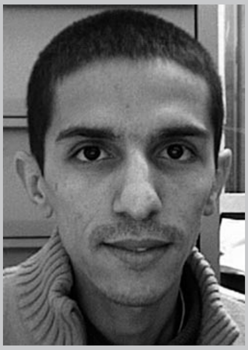
2. Neutral Rhodium and Iridium p-Benzoquinone Linkers

Quinones are considered a prominent class of compounds and play an important role in chemistry and biology.[28–31] Their biological action is often linked to their electron-transfer rates and redox behavior.[32] Quinone/hydroquinone redox couples have been widely used in electrochemical studies, because they are readily available and exhibit well-behaved electrochemistry.[33,34] Surprisingly, there are only a few examples of metal complexes in which hydroquinone or quinone acts as a π-bonded ligand.[35–39] Examples include η^4-quinone complexes of manganese tricarbonyl[40] and the related η^5-semiquinone complexes; however, the chromium analogue [$Cr(CO)_3(\eta^6$-hydroquinone)] was reported to be thermally unstable and air-sensitive and hence could not be isolated.[41,42] Thus, the nature of the metal and the auxiliary ligands plays an important role in stabilizing these quinone and hydroquinone complexes. In 1998, we reported the synthesis of the first stable iridium hydroquinone complex [Cp*Ir(η^6-hydroquinone)]$^{2+}$.[22,23] Subsequent deprotonation gave the related η^5-semiquinone and η^4-quinone compounds. The latter can be protonated to give the starting material (Schemes 2 and 3). More recently, we found an easier method to prepare the rhodium and iridium quinone complexes using the triflate ($CF_3SO_3^-$, OTf^-) salt [Cp*M(solvent)$_3$][OTf]$_2$[24] rather than the tetrafluoroborate ones, as shown below.

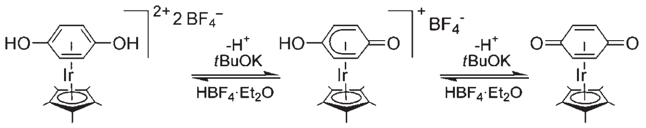


Scheme 2.

Hani, Haniel Amouri was born in Anapolis Goias (Brazil) and obtained his Ph.D. (1987) in chemistry with Professor John A. Osborn in homogeneous catalysis (hydrogenation) from Université Louis Pasteur Strasbourg (France). In 1988 he spent one year at Gif-sur-Yvette (France) as a postdoctoral fellow with Dr. Hugh Felkin, where he studied C–H activation of saturated hydrocarbons with transition-metal polyhydrides. In 1992–1993 he spent one year at University of California Berkeley with Professor Peter Vollhardt working on the synthesis of oligocyclopentadienyl metal complexes and their behavior as electron-transfer reagents. He is a Research Director in CNRS and currently is the director of the ARC group (Auto-assemblage, Reconnaissance et Chiralité) of the UMR-7071 at Université Pierre et Marie Curie (Paris). Among his research interests are chirality, organometallic, and supramolecular coordination chemistry.



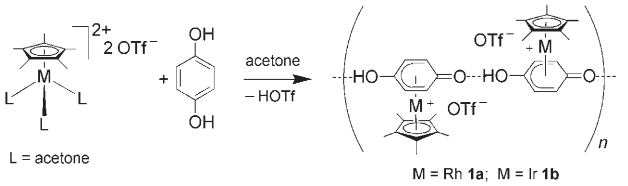
Jamal Moussa was born in 1978 in Oulad el Bali (Morocco) and obtained his M.Sc. degree (DEA) from Université Pierre et Marie Curie-Paris 6 in 2004. He joined the group of Dr. H. Amouri in 2003 to prepare his PhD in supramolecular coordination chemistry after obtaining a PhD grant from Ministères de Recherches et de la Technologie (MRT). His thesis work deals with self-assembly and photophysical properties of novel supramolecular architectures based on organometallic linkers.



Scheme 3.

2.1. One-Dimensional Rhodium and Iridium Semiquinones and Hydrogen Bonding

Treatment of hydroquinone with [Cp*Rh(solvent)$_3$][OTf]$_2$, prepared in situ in acetone from the rhodium dimer [{Cp*Rh(μ-Cl)Cl}$_2$] and AgOTf, provided the one-dimensional assembly [{{Cp*Rh(η^5-semiquinone)}(OTf)}$_n$] (**1a**), identified by spectroscopic data, microanalysis, and X-ray analysis (Scheme 4). The solid-state structure (Figure 2) shows the formation of an infinite 1D chain, in which simple {Cp*Rh(η^5-semiquinone)} subunits are connected through strong intermolecular hydrogen bonds. The hydrogen-bonded O···O separation of 2.46 Å (average) is remarkably short and can be compared to the O···O separation of 2.74 Å reported for the quinhydrone.[43]



Scheme 4. Synthesis of 1D [{{Cp*M(η^5-semiquinone)}(OTf)}$_n$]. M = Rh (**1a**), Ir (**1b**).

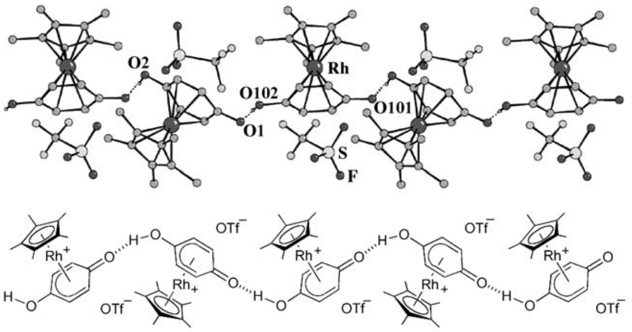


Figure 2. Crystal structure and structural formula of **1a**. H atoms not involved in hydrogen bonding are omitted for clarity.

The iridium semiquinone [{{Cp*Ir(η^5-semiquinone)}(OTf)}$_n$] (**1b**) was prepared in a similar way. The structure of **1b** is very close to that of **1a** and thus will not be presented herein.

2.2. p-Benzoquinone Rhodium and Iridium Linkers

As mentioned above, we have found that the rhodium and iridium polymers [{{Cp*M(η^5-semiquinone)}(OTf)}$_n$] (M = Rh, **1a**; M = Ir, **1b**) are good precursors for the related metal benzoquinone complexes [Cp*M(η^4-benzoquinone)] (M = Rh, **2a**; M = Ir, **2b**), which are prepared by deprotonation using Cs_2CO_3. The structures of **2a** and **2b** were confirmed by single-crystal X-ray diffraction studies (Figure 3). As expected, the {Cp*Rh} and {Cp*Ir} moieties are coordinated to only four carbon atoms of the quinone π system. Furthermore, the quinone ligand adopts a boat-like conformation, with the quinonoid carbon atoms bent out of the diene plane by about 12° for **2a** and 16° for the iridium congener **2b**.[23,24]

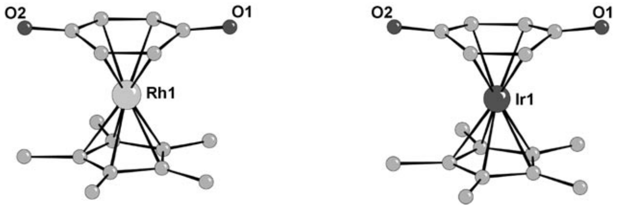


Figure 3. Crystal structures of **2a** (left) and **2b** (right).

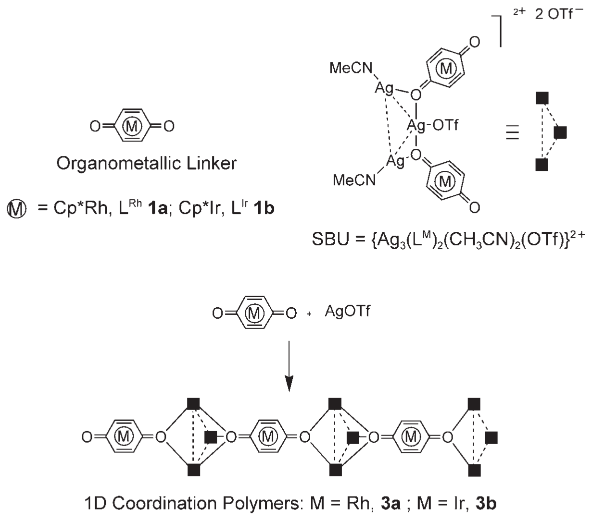
3. Supramolecular Coordination Assemblies with Coinage Metals

Supramolecular chemistry of coordination polymers has become an important research domain of modern inorganic chemistry. However, it is well-established that such assemblies are constructed from organic linkers and transition metals with different coordination geometries. Therefore, our approach is novel, because we use organometallic linkers **2a**–**e** that are suited to assemble a variety of supramolecular coordination polymers depending on the geometry, charge, and reactivity of the selected transition-metal subunit.

3.1. One-Dimensional Coordination Polymers with Secondary Building Units Featuring Ag···Ag Interactions

Treatment of [Cp*M(η^4-benzoquinone)] (M = Rh, **2a**; M = Ir, **2b**) with excess AgOTf in CH_2Cl_2 provided, after workup and crystallization from CH_3CN/Et_2O, golden or off-white crystals of 1D coordination polymers [{{$Ag_3(L^M)_2(CH_3CN)_2$(OTf)}(L^M)(OTf)$_2$}$_n$] (**3a**,**b**, Scheme 5).[44]

To ascertain the identity of these complexes, a single-crystal X-ray diffraction study was undertaken (Figure 4). The structures of both **3a** and **3b** reveal 1D coordination polymers. Compound **3b** consists of trinuclear silver nodes {$Ag_3(L^{Ir})_2(CH_3CN)_2$(OTf)}$^{2+}$ that are linked through linear η^4-benzoquinone ligand L^{Ir} (**2b**). In this linear coordination polymer, the trinuclear silver clusters constitute the so-called secondary building units (SBUs, Scheme 5).[45,46] In each SBU, all silver atoms have tetrahedral configurations. The central silver atom, Ag2, lies on a plane of symmetry and is coordinated to a triflate anion and to three quinone oxygen atoms. The other two silver atoms, which are symmetrically related, are linked to three quinone oxygen atoms and coordinated to CH_3CN (Scheme 5). The Ag2···Ag1 separation



Scheme 5. Self-assembly of 1D polymers **3a,b** showing the secondary building units (SBUs) connected by the pentacoordinating organometallic linkers L^{M} (M = Rh, **2a**; M = Ir **2b**).

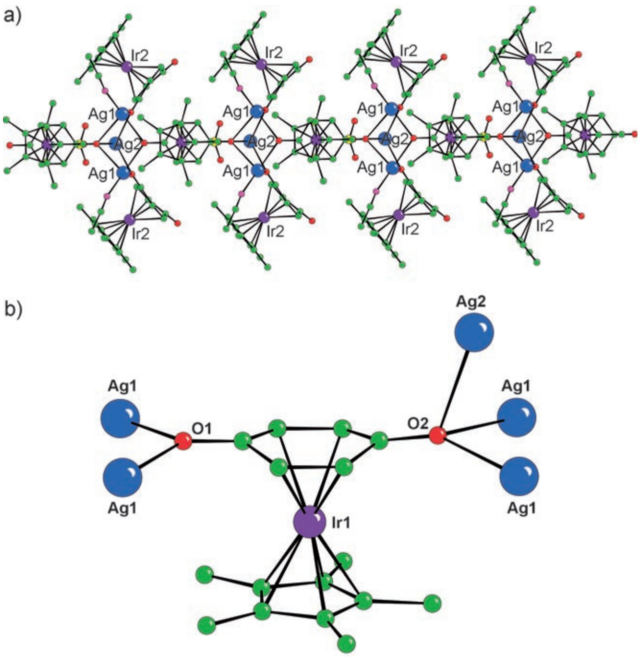


Figure 4. a) Crystal structure of **3b**; the free triflate anions and hydrogen atoms are omitted for clarity. b) View of the coordination environment of the pentacoordinating organometallic linker L^{Ir} in **3b**. Ag blue, Ir purple, N pink, O red, S yellow (coordinated triflate), C green.

between the central silver atom and the peripheral ones is 3.37 Å, indicative of interatomic contact (sum of the van der Waals radii of silver is 3.44 Å[47]), while the peripheral Ag1···Ag1 distance is 3.71 Å, suggesting a weak interaction. Interestingly, the organometallic linker L^{Ir} adopts a boat conformation in **3b**, with the quinone carbons bent out of the diene plane. The linker acts as a pentacoordinating ligand and connects five silver atoms such that one quinone oxygen atom is doubly bridging (hinge angle between the C=O bond and the plane formed by the diene carbon atoms $\theta = 11.85°$) and the other is triply bridging (hinge angle $\theta = 11.72°$). Such a coordination mode has not been reported before (Figure 4b).

Thus, each SBU is connected to the adjacent SBU through a doubly bridging quinone oxygen atom from one side and through a triply bridging quinone oxygen atom from the opposite side, thereby defining a unique architecture for the 1D coordination polymers $[\{\{Ag_3(L^{M})_2(CH_3CN)_2(OTf)\}(L^{M})(OTf)_2\}_n]$ (**3a**, **b**). The NMR spectra of these polymers in solution are useful to recognize the presence of their constituent building blocks, but they cannot give information about the extended arrays in the solid state.

In the examples above we have shown that, remarkably, these organometallic linkers act as pentacoordinating ligands in **3a,b**. We anticipated that, owing to the nature of the metal ions used, the coordination modes of the organometallic linker could be modified, as illustrated in the next section.

3.2. One-Dimensional Zigzag Coordination Polymer with Iridium Linkers and Copper Ions

Treatment of $[Cp^{*}Ir(\eta^{4}\text{-benzoquinone})]$ (**2b**) with the air-sensitive complex of copper(I) triflate and benzene $[(CuOTf)_2(C_6H_6)]$ in CH_2Cl_2 resulted in a suspension. The product was recrystallized from CH_3CN/diethyl ether to give golden crystals of $[\{\{Cu_2(L^{Ir})_2(CH_3CN)(OTf)_2\}(L^{Ir})(OTf)\}_n]$ (**4**). To ascertain the identity of this complex, a single-crystal X-ray diffraction study was undertaken (Figure 5). The structure of **4** shows the formation of a 1D zigzag coordina-

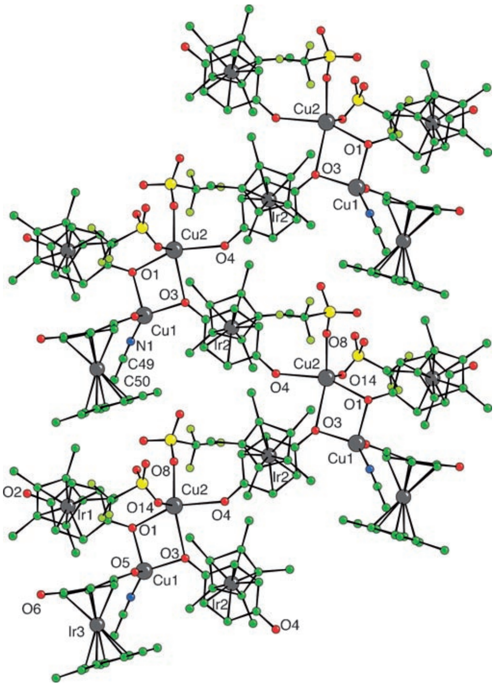
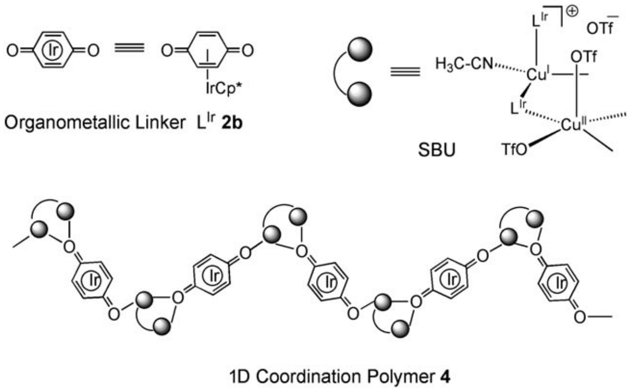


Figure 5. Crystal structure of the cationic part of the zigzag 1D coordination polymer **4**. H atoms are omitted for clarity. Cu gray, N blue, O red, S yellow, F green-yellow, C green.

tion polymer.[48] It consists of SBUs of the formula $\{Cu_2(L^{Ir})_2(CH_3CN)(OTf)_2\}^+$ that are linked through the η^4-benzoquinone ligand L^{Ir} (**2b**) in a zigzag fashion (Scheme 6).



Scheme 6. Self-assembly of 1D zigzag coordination polymer **4**.

Each SBU consists of one Cu^I center with tetrahedral coordination and one Cu^{II} center with square-pyramidal coordination. The Cu^{II} center is coordinated to two triflate anions and to three quinone oxygen atoms, while the Cu^I center is linked to three quinone oxygen atoms and one CH_3CN molecule (Scheme 6). The $Cu^I\cdots Cu^{II}$ separation is 3.5 Å, too long for interatomic contact (sum of van der Waals radii of Cu is 2.80 Å[47]). Interestingly, the organometallic linker L^{Ir} adopts a boat conformation in **4**, with the quinone carbon atoms bent out of the diene plane. It acts as a tricoordinating ligand and connects three copper atoms such that one quinone oxygen is bridging (hinge angle $\theta = 10.70°$) and the other is terminal (hinge angle $\theta = 17.29°$; Figure 5). The SBUs in **4** are thus connected through a bridging quinone oxygen atom of the organometallic linker L^{Ir} from one side and through a terminal quinone oxygen atom from the opposite side, resulting in a unique architecture for the 1D zigzag coordination polymer **4**. During the formation of **4**, the air-sensitive starting material $[(CuOTf)_2(C_6H_6)]$ is partially oxidized to give some Cu^{II} ions in solution, which are self-assembled in the presence of starting material CuOTf to give the target supramolecular assembly **4**; $[(CuOTf)_2(C_6H_6)]$ is well-known to disproportionate in solution to give Cu^0 and Cu^{II} ions.[49]

On the other hand, we have found that the iridium linker **2b** is more stable than its congener **2a**, since no supramolecular assembly could be formed with **2a** with copper ions. To understand the self-assembly process and to avoid the partial oxidation of the metal ion that led to **4**, we repeated the previous example but using the stable coinage-metal compound AgOTf instead. The results are discussed below.

3.3. Two-Dimensional Assemblies of Metallamacrocycle Chains with Iridium Linkers

Reaction of $[Cp^*Ir(\eta^4\text{-benzoquinone})]$ (**2b**) with AgOTf in CH_2Cl_2 and subsequent recrystallization from CH_3CN/diethyl ether provided colorless crystals of **5**, which were subjected to single-crystal X-ray diffraction analysis.

The structure (Figure 6) shows a 2D coordination network that results from weak edge-to-face π stacking between the hydrogen atoms of the Cp* methyl groups of one 1D coordination chain and the aromatic ring of another metalated $\{\eta^5\text{-}Cp^*Ir\}$ moiety of another 1D coordination chain.[48] The hydrogen atoms are located 2.7–2.8 Å from the center of the corresponding ring. This separation is within the typical range of C–H–π interactions.[50,51] Each 1D coordination chain can be better described as chains of metallamacrocycles comprising a 14-membered ring fused to a 4-membered ring. In this supramolecular assembly, the η^4-quinone ligand is coordinated to the silver ions through the oxygen atoms. Each silver ion is tetrahedrally coordinated by three oxygen atoms and one CH_3CN ligand. Similar to **4**, one of the oxygen atoms of the η^4-quinone ligand binds to two silver ions, while the other oxygen atom coordinates to only one metal center. The $Ag\cdots Ag$ distance is 3.638 Å, suggesting a weak argentophilic interaction. Analogous to **4**, the η^4-benzoquinone unit in **5** adopts a boat conformation with hinge angles $\theta = 22.4°$ for the terminal oxygen atom and $\theta = 15.9°$ for the bridging oxygen atom. As a result, the C=O carbon atoms are not coordinated to the Cp*Ir moiety. In contrast, the diene carbon atoms are strongly coordinated to the metal center, so that the overall structure is best described as an η^4-quinone. The bridging benzoquinone rings in **5** are arranged face-to-face at a short distance 3.17 Å but their mutual tilt angle $\varphi = 44°$, thus excluding any π–π interactions, with the bulky $\{\eta^5\text{-}Cp^*Ir\}$ moieties pointing away from the benzoquinone in this 2D network.

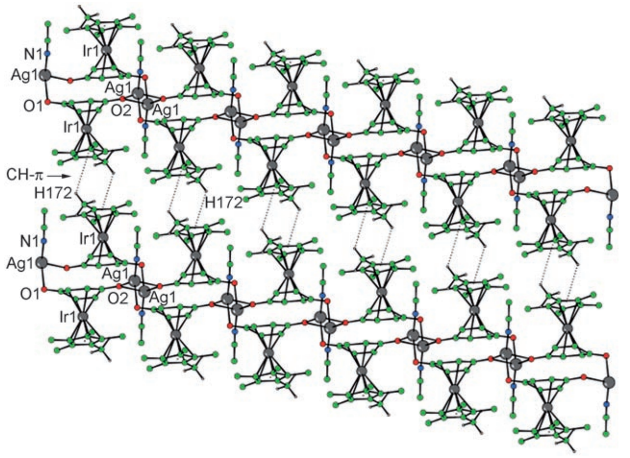


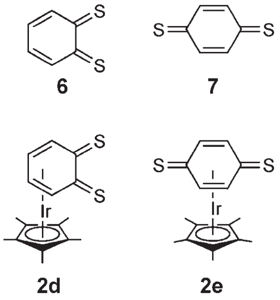
Figure 6. Crystal structure of the cationic part of the 2D network **5**. H atoms not involved in C–H–π interactions are omitted for clarity.

Although in **4** and **5** the organometallic linker is a tricoordinating ligand, the structure of **5** is intrinsically different from that of **4**. A simple comparison of the ratio L^{Ir}/coinage metal in **4** (3:2) and in **5** (1:1) shows this difference. Furthermore, we attribute the difference between the two supramolecular assemblies **4** and **5** to the geometrical preference of the Cu^{II} ions, which adopt a square pyramidal geometry, in contrast to the tetrahedrally coordinated Cu^I and Ag^I ions.

These results illustrate our successful approach to constructing new supramolecular assemblies using organometallic ligand linkers L^M capable of attaching different metal ions of different geometries within a well-defined superstructure. To extend these studies, we sought other organometallic linkers and turned to metalated thioquinonoids. Because the sulfur atoms are soft centers, in contrast to the hard oxygen centers, we anticipate that the coordination chemistry of the new organometallic linkers with sulfur nucleophiles will be highly interesting and challenging.

4. Neutral Iridium o- and p-Dithiobenzoquinone Linkers

Although the chemistry of *o*- and *p*-benzoquinone is well-documented,[52] very little is known about the related *o*- and *p*-dithiobenzoquinone (**6** and **7**, Scheme 7). Unlike benzoquinones, the sulfur analogues are highly reactive, making their handling and isolation in pure form difficult.[53,54] Therefore, examples of isolated thioquinones are scarce; in fact, *p*-dithiobenzoquinone (**7**) has been generated and characterized spectroscopically only at low temperature (10 K) in an argon matrix, because it is extremely reactive and was observed to decompose in an unknown manner on moderate warming of the matrix.[55]



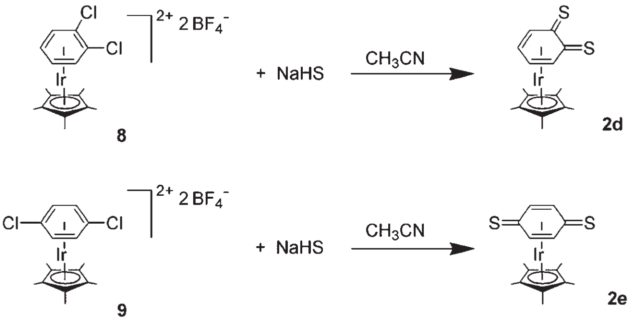
Scheme 7. The *o*- and *p*-dithiobenzoquinones **6** and **7** and the related metal complexes **2d** and **2e**.

The isomeric *o*-dithiobenzoquinone (**6**) has proven even more elusive. Three attempts to generate this compound have been recorded. 1) The matrix-isolated product from pyrolysis of 1,3-benzodithiol-2-one showed an ultraviolet spectrum suggestive of the transient benzodithiete rather than that expected of *o*-dithiobenzoquinone (**6**).[56] 2) The photolysis of the same starting material also did not afford **6** as an isolable product, but its transient generation was demonstrated by trapping it with dimethylacetylenedicarboxylate to give 2,3-bis(carbomethoxy)-1,4-benzodithiin in modest yield.[57] 3) Finally, the diaminodithioquinone approach of Perkin and Green did not yield the elusive monomeric dithione (**6**) either; instead, a polymeric species featuring disulfide bonds was proposed.[58] All of these procedures illustrate the difficulty in isolating and stabilizing *o*- and *p*-dithiobenzoquinones **6** and **7**.

4.1. Synthesis of o- and p-Dithiobenzoquinone as Metal Complexes

Recently, we discovered a synthetic procedure to isolate the first stable η^4-*o*- and *p*-dithiobenzoquinone complexes (Scheme 7). The parent compounds were obtained as iridium complexes $[Cp^*Ir(\eta^4\text{-}o\text{-}C_6H_4S_2)]$ (**2d**) and $[Cp^*Ir(\eta^4\text{-}p\text{-}C_6H_4S_2)]$ (**2e**) and were fully characterized, including by the first X-ray molecular structure of **7** as a metal complex.

In previous work, we reported the first example of metal-stabilized *o*-quinone methide and showed that {Cp*Ir} can stabilize this highly reactive intermediate through η^4-coordination to the internal diene moiety of the simple quinone methide.[59] Pursuing our research in this area, that is, stabilization of reactive intermediates,[60,61] we discovered that {Cp*Ir} can also stabilize the elusive *o*- and *p*-dithiobenzoquinone intermediates.[25] Our synthetic approach is completely different from that reported for the quinone methide. It involves the synthesis of halogenated 1,2- and 1,4-dichloro arene π complexes $[Cp^*Ir(\eta^6\text{-}o\text{-}C_6H_4Cl_2)][BF_4]_2$ (**8**) and $[Cp^*Ir(\eta^6\text{-}p\text{-}C_6H_4Cl_2)][BF_4]_2$ (**9**), which are the key molecules for **2d** and **2e**. Subsequent substitution of the chlorides by HS^- provided the target compounds **2d** and **2e** in high yields (Scheme 8).



Scheme 8. Synthesis of the organometallic linkers **2d** and **2e**.

4.2. X-ray Crystal Structure of Metal-Stabilized p-Dithiobenzoquinone

The structure of the dithiobenzoquinone complex **2e** was confirmed by a single-crystal X-ray diffraction study (Figure 7). The structure of **2e** clearly shows that the {Cp*Ir} moiety is coordinated only to the four diene carbon atoms of

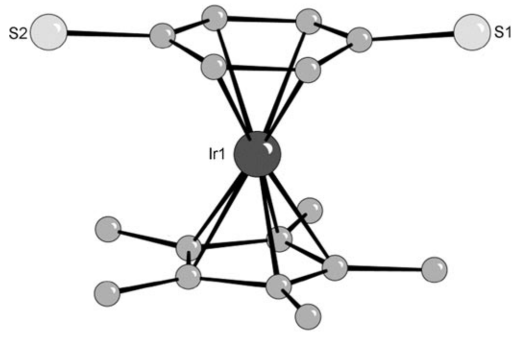
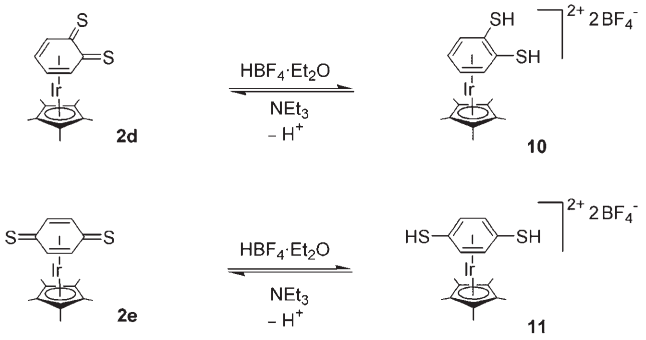


Figure 7. Crystal structure of $[Cp^*Ir(\eta^4\text{-}p\text{-}C_6H_4S_2)]$ (**2e**).

the π-thioquinone ligand. Furthermore, the η^4-thioquinone ligand acquires a boat-like conformation similar to that observed for the analogous iridium benzoquinone complex.[23] To our knowledge, this is the first X-ray structure of the parent thioquinone complex reported in the literature.

Protonation of a suspension of either **2d** or **2e** in CH_3CN by $HBF_4{\cdot}Et_2O$ provided the related dithiophenol complexes $[Cp^*Ir\{\eta^6\text{-}o\text{-}C_6H_4(SH)_2\}][BF_4]_2$ (**10**) or $[Cp^*Ir\{\eta^6\text{-}p\text{-}C_6H_4(SH)_2\}][BF_4]_2$ (**11**; Scheme 9). Complexes **10** and **11** react with NEt_3 to regenerate **2d** and **2e**, respectively.



Scheme 9. Protonation–deprotonation reactions.

To understand the role of {Cp*Ir} in stabilizing the short-lived *p*-dithiobenzoquinone, we have taken an ab initio computational approach employing the hybrid density functional B3LYP. Computational analyses using density functional theory confirm a net transfer of about 0.8 units of electron density to the ligand π* lowest unoccupied molecular orbital (LUMO) and 0.2 units of electron density to each sulfur atom. This additional electron density is largely localized around the thiocarbonyl bonds, resulting in a reduction in C=S bond order as well as the anticipated decrease in C=C bond order. These calculations also indicate that the sulfur atoms in the metalated thioquinone $[Cp^*Ir(\eta^4\text{-}p\text{-}C_6H_4S_2)]$ (**2e**) are more nucleophilic, thus making the parent complexes good organometallic ligands to construct supramolecular structures with transition-metal electrophiles, as shown in the next section.

5. Supramolecular Coordination Assemblies Featuring Pt···Pt and π–π Interactions

5.1. A One-Dimensional Supramolecular Assembly from {Pt(2,2′-bipyridine)} and o-Dithiobenzoquinone Linker

Reaction of $[Cp^*Ir(\eta^4\text{-}o\text{-}C_6H_4S_2)]$ (**2d**) with $[PtCl_2(bpy)]$ (bpy = 2,2′-bipyridine) in CH_3CN in the presence of AgOTf gave a new compound, which was fully characterized as $[Pt(bpy)\{Cp^*Ir(\eta^4\text{-}o\text{-}C_6H_4S_2)\}][OTf]_2$ (**12**). The X-ray crystal structure of **12** was also determined, and the cationic part of the complex is shown in Figure 8a. The structure of **12** shows that the *o*-dithiobenzoquinone iridium complex indeed chelates the {Pt(bpy)} fragment through the two sulfur atom such that the coordination geometry around the Pt center is square-planar. Because of this coordination mode, the aromatic ring of the *o*-thioquinone is planar and symmetrically (η^6) bound to the {Cp*Ir} moiety.

Further examination of the crystal packing of **12** reveals that the molecules are stacked in a head-to-tail orientation with π–π interactions between adjacent bipyridyl ligands (d = 3.484, 3.669 Å) and indicates the presence of Pt···Pt interactions (d = 3.574 Å). These Pt···Pt and π–π interactions occur in an alternate fashion between the individual molecules of $[Pt(bpy)\{Cp^*Ir(\eta^4\text{-}o\text{-}C_6H_4S_2)\}]^{2+}$, resulting in a 1D supramolecular chain.[62] In this assembly, each square-planar $\{Pt(bpy)S_2\}$ subunit is rotated by 38.54° relative to the adjacent molecule. Other platinum(II) polypyridyl complexes have shown similar extended linear chain packing.[63] This result prompted us to investigate a similar reaction using the *p*-thiobenzoquinone metal complex **2e** as the organometallic linker.

5.2. One-Dimensional Supramolecular Assembly from {Pt(2,2′;6′2″-terpyridine)} and p-Dithiobenzoquinone Linker

As mentioned above, to achieve a successful supramolecular coordination assembly, it is very important to select a perfect match between the structure of the assembling ligand and the preferred geometry of the electrophilic metal center. In this example, our organometallic linker **2e** has a linear form in which the two nucleophilic sulfur sites are 180° from each other, and therefore it cannot chelate a $\{Pt(bpy)\}^{2+}$

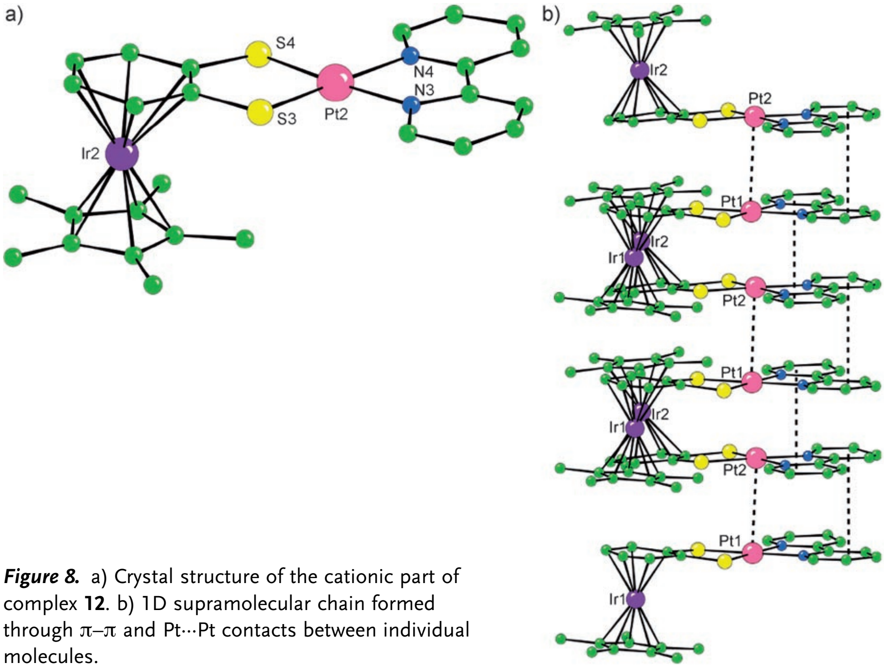


Figure 8. a) Crystal structure of the cationic part of complex **12**. b) 1D supramolecular chain formed through π–π and Pt···Pt contacts between individual molecules.

electrophile. Thus, we instead chose the platinum electrophilic building block $\{Pt(terpy)\}^{2+}$ (terpy = 2,2′;6′2″-terpyridine), which has only one available site for coordination.

Treatment of **2e** with two equivalents of [Pt(terpy)Cl]Cl in CH_3CN in the presence of AgOTf provided an orange complex that was identified as a 1D supramolecular assembly, $[\{\{Pt(terpy)\{Cp^*Ir(\eta^4\text{-}p\text{-}C_6H_4S_2)\}Pt(terpy)\}(OTf)_4\}_n]$ (**13**). The X-ray crystal structure of **13** was determined, and the cationic part of the complex is shown in Figure 9a. The structure of **13** shows that the *p*-dithiobenzoquinone iridium complex bridges two {Pt(terpy)} fragments through the two sulfur centers with two equal Pt–S bond lengths of 2.330 Å. In this Pt–Ir–Pt supramolecular system, the {Pt(terpy)} units can be described as two large wings of a butterfly of which the main body is defined by the *p*-dithiobenzoquinone complex $[Cp^*Ir(\eta^4\text{-}p\text{-}C_6H_4S_2)]$. The coordination geometry around each Pt center is square-planar, formed by three nitrogen atoms of the terpy ligand and one sulfur center from the bridging organometallic linker **2e**. Because of this coordination mode, the C_6 ring of the organometallic linker **2e** is not quite planar, with the C=S carbon atoms bent out of the diene plane. The linker acts as a bridging ligand and connects two Pt^{II} atoms such that each thioquinone sulfur atom is terminally coordinated to Pt. The hinge angles ($\theta(S1) = 7.7°$, $\theta(S2) = 5.6°$) are smaller than those reported for the free organometallic linker **2e**.

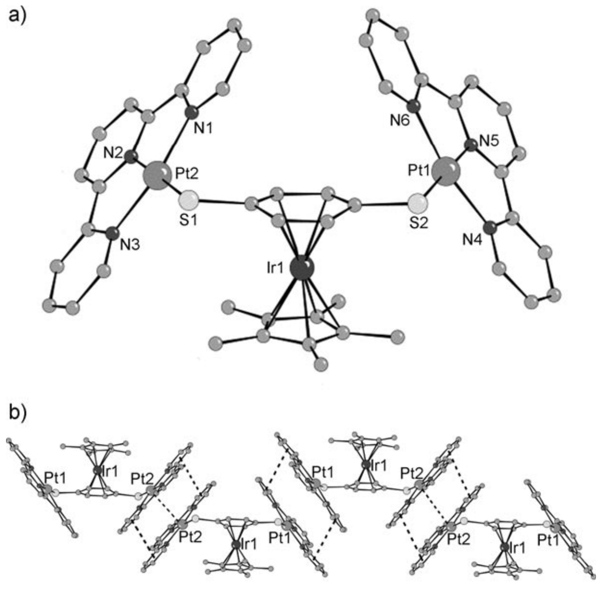


Figure 9. a) Crystal structure of the cationic part of complex **13**. b) 1D supramolecular chain formed through π–π and Pt···Pt contacts between individual molecules.

The two {Pt(terpy)} wings in **13** are not linearly disposed but are puckered and lean backward with a Pt1···Pt2 separation of 8.088 Å. Analysis of the crystal packing of **13** reveals that the molecules are stacked in a head-to-head and tail-to-tail fashion with two sets of π–π and Pt2···Pt2 interactions between each side of one {Pt(terpy)} arm and the adjacent molecule. For instance, the first {Pt(terpy)} unit interacts with an adjacent {Pt(terpy)} fragment through a π–π interaction ($d = 3.461$ Å, $\varphi = 25.07°$), while the Pt1···Pt1 separation is 4.037 Å, which is too long to suggest interaction. The other {Pt(terpy)} arm forms a stronger π–π interaction with an adjacent {Pt(terpy)} unit ($d = 3.385$ Å, $\varphi = 20.24°$) and exhibits a weak Pt2···Pt2 contact (3.596 Å). These Pt···Pt and π–π interactions between individual subunits of **13** construct a 1D supramolecular chain. Other platinum(II) complexes have shown similar extended linear chain packing.[64–68]

To our knowledge, complexes **12** and **13** were first examples of 1D supramolecular chains of {Pt(bpy)} and {Pt(terpy)} subunits assembled by the organometallic linkers **2d** and **2e**. This class of coordination networks exhibited interesting photoluminescence properties arising from this unusual coordination, which induces Pt···Pt and π–π interactions along the 1D chain (Figure 9b).[27]

6. Summary and Outlook

Herein, we summarize our recent reports concerning the self-assembly of a new class of supramolecular coordination architectures with organometallic linkers, the construction of which relies on a new concept. The basic idea is to use the designed metalated quinonoid compounds $[Cp^*M(C_6H_4O_2)]$ (M = Rh, Ir) and the related *o*- and *p*-thioquinonoid complexes of the type $[Cp^*Ir(C_6H_4S_2)]$ as bridging ligands. In fact, owing to the back-donation of the {Cp*M} unit, the oxygen or sulfur atoms in these stable organometallic linkers are now more nucleophilic and hence capable of binding to electrophilic metal centers. This concept was applied to generate a variety of supramolecular architectures employing the above organometallic linkers and with electrophilic metal building blocks of different geometrical shapes, such as Ag^I, Cu^{II}, $\{Pt(bpy)\}^{2+}$, and $\{Pt(terpy)\}^+$. These supramolecular assemblies exhibit noncovalent interactions such as π stacking, metal–metal interactions, and the formation of secondary building blocks that self-assemble to provide unique coordination networks. This new field merges the principles of supramolecular chemistry, coordination chemistry, and organometallic chemistry for the generation of an impressive range of novel supramolecular architectures. The proof of principle has been achieved, and the concept can now be used to develop new bridging organometallic linkers that could be used to generate chiral coordination networks.

We would like to thank CNRS and Université Pierre et Marie Curie-Paris 6 for supporting this work.

Received: May 4, 2007
Revised: June 25, 2007

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