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ortho- and *para*-Thioquinonoid π-Complexes: First Synthesis, Reactivity, and Crystal Structure Determination

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Overcoming a long-standing challenge, the *o*- and *p*-dithiobenzoquinone iridium complexes [Cp*Ir-*o*-(η^4-$C_6H_4S_2$)] (**6**) and [Cp*Ir-*p*-(η^4-$C_6H_4S_2$)] (**7**) were rationally synthesized and fully characterized for the first time including the X-ray molecular structure of [Cp*Ir-*p*-(η^4-$C_6H_4S_2$)] (**7**). Our strategic approach involves the preparation of the halogenated 1,2- and 1,4-dichloro arene π complexes [Cp*Ir-*o*-(η^6-$C_6H_4Cl_2$)][BF_4]$_2$ (**4**) and [Cp*Ir-*p*-(η^6-$C_6H_4Cl_2$)][BF_4]$_2$ (**5**), which are the key molecules for **6** and **7**. Subsequent treatment of **4** and **5** with NaSH and halogen displacement provides the target thioquinonoid π complexes **6** and **7** in 88 % and 95 % yields respectively. Further, the coordination chemistry of the *o*-dithiobenzoquinone iridium complex [Cp*Ir-*o*-(η^4-$C_6H_4S_2$)] (**6**) was studied by treating **6** with [(bpy)$PtCl_2$] in the presence of AgOTf, which provided the novel platinum complex [Pt(bpy){Cp*Ir-*o*-(η^4-$C_6H_4S_2$)}][OTf]$_2$ (**10**) in 91 % yield. The X-ray molecular structure of **10** is reported and shows as outstanding features the formation of 1D supramolecular assembly, which results from π–π (d = 3.484 Å; d = 3.669 Å) and Pt···Pt (d = 3.574 Å) interactions between individual subunits.

Introduction

Although the chemistry of *o*- and *p*-benzoquinone is well documented,[1] very little is known about the related *o*- and *p*-dithiobenzoquinone (**1**, **2**) (Figure 1). Unlike benzoquinones, the sulfur analogues are highly reactive owing to their instability, making their handling and isolation in pure form a difficult task. Thus examples of isolated thioquinones are scarce and in fact *p*-dithiobenzoquinone (**2**) 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.[2] Recently Oda and co-workers reported the synthesis of 2,6-di-*tert*-butyl-1-thio-1,4-benzoquinone, where the presence of two *tert*-butyl groups at the 2- and 6-positions offers steric protection and increases the stability of the mono-thiobenzoquinone.[3] More recently, Cava and co-workers reported the synthesis of dithioanthraquinone analogue in 16% yield by several steps: first annelation of thiophene rings to benzoquinone produced the anthraquinone analogue, and subsequent treatment with Lawesson's reagent and/or Davy reagent methyl for 18 h produced the mono- and dithio-anthraquinone analogues.[4] However, none of the previous attempts allowed the isolation of *p*-dithiobenzoquinone (**2**).

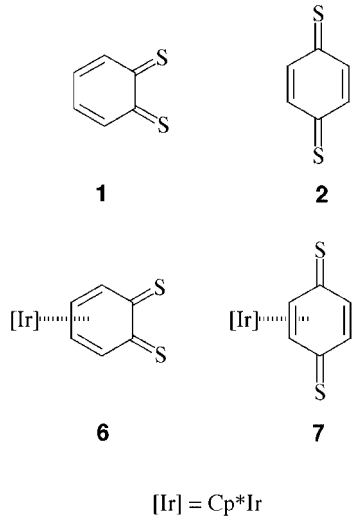

Figure 1. *o*- and *p*-dithiobenzoquiones complexes.

The isomeric *o*-dithiobenzoquinone (**1**) has proven to be even more elusive. Three attempts to generate this compound have been recorded. (i) 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 (**1**).[5] (ii) The photolysis of the same starting material 1,3-benzodi-

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thiol-2-one also did not afford **1** as an isolable product but its transient generation was proven by trapping it with dimethyl acetylenedicarboxylate to give dimethyl 1,4-benzodithiin-2,3-dicarboxylate in moderate yield.[6] (iii) Finally, Perkin and Green's diaminodithioquinone approach did not yield the monomeric elusive dithione (**1**) either; instead a polymeric species featuring disulfide bonds was proposed.[7] All these procedures illustrate the difficulty in isolating and stabilizing *o*- and *p*-dithiobenzoquinones (**1**, **2**).

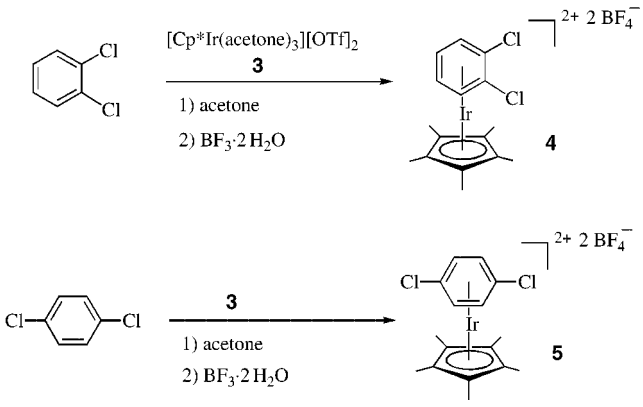
In contrast, here we report a rational synthetic procedure to isolate and fully characterize the first stable η^4-dithio-*o*- and -*p*-benzoquinone complexes (**6**, **7**) (Figure 1). The parent compounds were obtained as iridium complexes [Cp*Ir-*o*-(η^4-$C_6H_4S_2$)] (**6**) and [Cp*Ir-*p*-(η^4-$C_6H_4S_2$)] (**7**) and were fully characterized including the first X-ray molecular structure of the dithio-*p*-benzoquinone as a metal complex **7**.

In a previous work we reported the first example of metal-stabilized *o*-quinone methide, and showed that the Cp*Ir can stabilize this highly reactive intermediate through η^4-coordination to the internal diene moiety of the simple quinone methide.[8] Pursuing our research in this area, that is, stabilization of reactive intermediates,[9] we discovered that Cp*Ir can also stabilize the elusive *o*- and *p*-dithiobenzoquinone intermediates; a previous communication on the stabilization of **2** has recently been published.[10] Our synthetic approach is completely different to that reported for the quinone methide. It involves the synthesis of halogenated 1,2- and 1,4-dichloroarene π complexes [Cp*Ir-*o*-(η^6-$C_6H_4Cl_2$)][BF_4]$_2$ (**4**) and [Cp*Ir-*p*-(η^6-$C_6H_4Cl_2$)][BF_4]$_2$ (**5**), which are the key molecules for **6** and **7**. Subsequent substitution of the chlorides by (HS^-) provided the title compounds [Cp*Ir-*o*-(η^4-$C_6H_4S_2$)] (**6**) and [Cp*Ir-*p*-(η^4-$C_6H_4S_2$)] (**7**) in high yields (Figure 1).

Results and Discussion

Synthesis and Characterization of the Halogenated Arene π Complexes 4, 5 and Their Related *o*- and *p*-η^4-Dithiobenzoquinones 6, 7

We recently discovered that the π complexing ability of the Cp^*Ir^{2+} moiety is dramatically enhanced towards electron-poor halogenated arenes when the reaction is conducted in $BF_3{\cdot}2H_2O$ solution. These experimental conditions allow a smooth and efficient complexation of highly electron-deficient aromatics. Thus treatment of an excess of *o*- and/or *p*-dichlorobenzene with the solvated iridium complex [Cp*Ir(acetone)$_3$][OTf]$_2$ (**3**) in $BF_3{\cdot}2H_2O$ solution gave the iridium complexes [Cp*Ir-*o*-(η^6-$C_6H_4Cl_2$)][BF_4]$_2$ (**4**) and [Cp*Ir-*p*-(η^6-$C_6H_4Cl_2$)][BF_4]$_2$ (**5**) quantitatively as white microcrystalline complexes (Scheme 1). These air- and moisture-sensitive compounds were completely characterized. The ^{1}H NMR spectra recorded for **4** and **5** in CD_3NO_2 were similar, for instance, to the *ortho* complex **4**, which showed the presence of two doublets of doublets at δ = 7.52 and 7.83 ppm attributed to the aromatic protons and another singlet at δ = 2.35 ppm attributed to the methyl protons of Cp*Ir. In a similar fashion the *para* isomer **5** gave a singlet at δ = 7.82 ppm assigned to the ring protons and at δ = 2.48 ppm attributed to the methyl protons of Cp*Ir. The ^{19}F NMR spectra of both complexes showed a singlet at –152.7 ppm for **4** and at –153.6 ppm for **5** designated to the free BF_4 anion.[11] Further, the infrared spectra also showed a large band at 1083 cm^{-1} attributed to BF_4 anions. The ^{13}C NMR spectrum is in agreement with the proposed formula (see Experimental Section). As mentioned before, compounds **4** and **5** were very air- and moisture-sensitive and hence were kept under argon at low temperature because of the lability of the C–Cl bond of the coordinated arenes.

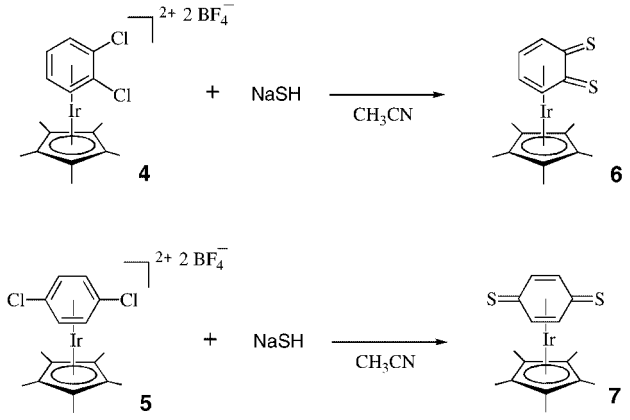


Scheme 1.

We then treated the white powder complexes **4** and **5** with an excess of dried NaSH in CH_3CN for 20 min. Reaction workup provided the neutral *o*- and *p*-η^4-dithiobenzoquinone complexes [Cp*Ir-*o*-(η^4-$C_6H_4S_2$)] (**6**) and [Cp*Ir-*p*-(η^4-$C_6H_4S_2$)] (**7**). Compounds **6** and **7** were obtained as red and orange microcrystalline materials, analytically pure and stable under argon. For instance, the infrared spectrum of **6** recorded in KBr discs displayed a sharp band at 1085 cm^{-1}, while that of **7** gave a band at 1096 cm^{-1}, which we attribute to C=S vibration. This thiocarbonyl stretching frequency is lower than that of the free monothio-1,4-benzoquinone (1141 cm^{-1}).[3] Such a trend has been observed for the C=O vibration in the related free and metallated 1,4-benzoquinone.[12] It is worth mentioning that infrared data for *o*- and *p*-dithiobenzoquinone complexes have not been reported before. All attempts to obtain crystals of *o*-dithiobenzoquinone metal complex **6** for an X-ray study were not successful, however we were able to obtain crystals of the *p*-isomer [Cp*Ir-*p*-(η^4-$C_6H_4S_2$)] (**7**) and the structure was determined (vide infra).

The structure of the *p*-dithiobenzoquinone [Cp*Ir-*p*-(η^4-$C_6H_4S_2$)] (**7**) was confirmed by a single-crystal X-ray diffraction study (Scheme 2). Crystals of **7** were grown by vapor diffusion of diethyl ether into a solution of the complex in CH_2Cl_2. Complex **7** crystallizes in the monoclinic unit cell with space group $P2_1/m$ with Z = 2. The asymmetric unit consists of three half complexes (I, II, and III), which are totally generated by crystallographic mirror planes and one molecule of CH_2Cl_2 with 25% occupation.

Molecules I and II show π–π interactions between (a) the η^5-Cp*Ir moiety of molecule I and the η^4-(S–C_6H_4–S) unit of another thioquinone metal complex (II) with d = 3.565(4) Å and α = 21.30(12)° and (b) the η^5-Cp*Ir moiety of molecule II and the η^4-(S–C_6H_4–S) unit of another thioquinone metal complex (I) with d = 3.631(3) Å and α = 17.69(15)°, providing a one-dimensional supramolecular chain (Figure 2, a).



Scheme 2. X-ray molecular structures of *p*-dithiobenzoquinone [Cp*Ir-*p*-(η^4-$C_6H_4S_2$)] (**7**) and [Pt(bpy){Cp*Ir-*o*-(η^4-$C_6H_4S_2$)}]-[OTf]$_2$ (**10**).

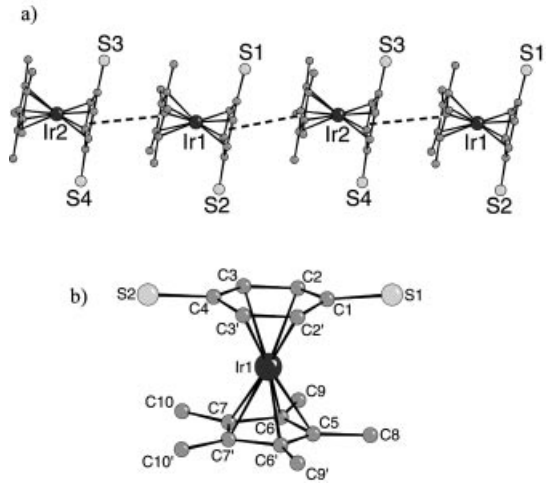
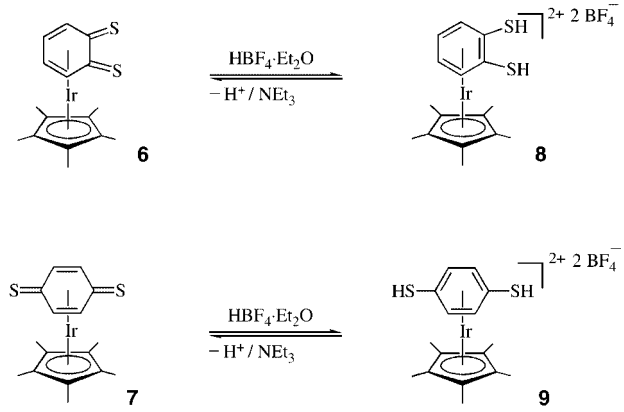


Figure 2. X-ray molecular structure of *p*-dithiobenzoquinone complex [Cp*Ir-*p*-(η^4-$C_6H_4S_2$)] (**7**). (a) 1D supramolecular chain formed through π–π contacts between molecules I and II. (b) Selected bond lengths [Å] and angles [°] for **7** molecule I: Ir1···C1 2.353(8), Ir1···C2 2.210(6), Ir1···C3 2.219(5), Ir1···C4 2.346(7), C1···S1 1.726(10), C4···S2 1.713(9), C2–C1–C2′ 114.2(9), C3–C4–C3′ 115.0(8).

The distance between the closest sulfur atoms of two independent molecules II and III is 4.23 Å, suggesting the absence of an interatomic contact (sum of van der Waals radii of sulfur is 3.7 Å).[13] A view of complex **7** with selected bond lengths and angles is shown in Figure 2b. The structure of **7** clearly shows the Cp*Ir moiety is coordinated to only four diene carbons of the π-thioquinone ligand. For instance the average values of the Ir–C distances are 2.367, 2.358 Å longer than those of the diene subunit (average bond lengths of 2.206, 2.214 Å) in molecules I, II and III. Further, the η^4-thioquinone ligand acquires a boat-like conformation with the thioquinoid carbons bent out of the diene plane by θ = 8.22(0.7)° and θ = 8.21(0.4)° in molecule I, while in molecule II the two dihedral angles are θ = 8.49(0.6)°, θ = 7.69(0.3)°, and θ = 12.94 (0.8) and θ = 10.04(1.1) in molecule III. These angle values are smaller than those reported for the analogous iridium benzoquinone complex (θ = 16°).[12a] The C–S bond lengths for the three independent molecules (I, II, III) are 1.719, 1.705, and 1.710 Å, which on average is 1.711 Å and characteristic of a partial double bond character (vide infra). This bond length is shorter than the simple C–S bond of 1.796 Å reported for 1,4-benzenedithiol[14] and 1.766 Å for 4,4′-biphenyldithiol,[15] but comparable to C=S bond lengths of 1.674–1.702 Å reported for several thiourea compounds.[16] To the best of our knowledge this is the first X-ray structure of the parent thioquinone complex reported in the literature.

Protonation of a suspension of either [Cp*Ir-*o*-(η^4-$C_6H_4S_2$)] (**6**) or [Cp*Ir-*p*-(η^4-$C_6H_4S_2$)] (**7**) in CH_3CN by $HBF_4{\cdot}Et_2O$ provided a rapid color change, giving rise to a red solution for **6** and yellow solution for **7**. Reaction work-up allowed the isolation of the related dithiophenol complexes [Cp*Ir-*o*-(η^6-HS–C_6H_4–SH)][BF_4]$_2$ (**8**) or [Cp*Ir-*p*-(η^6-HS–C_6H_4–SH)][BF_4]$_2$ (**9**) in 95% and 93% yields respectively as red and pale yellow microcrystalline solids (Scheme 3).



Scheme 3.

Compound **9** was characterized by spectroscopic data (^{1}H, IR). For instance the ^{1}H NMR of **9** recorded in CD_3CN showed the presence of a singlet at δ = 1.98 ppm attributed to the methyl protons of η^5-Cp*Ir and another singlet at δ = 7.15 ppm assigned to the aromatic protons that integrate to four protons. In a similar way complex **8** showed one singlet at δ = 2.10 ppm and two doublet of doublets at δ = 6.83 and 7.70 ppm, respectively. Upon treatment of the NMR tube sample of **9** in CD_3CN with NEt_3, the starting material [Cp*Ir-*p*-(η^4-$C_6H_4S_2$)] (**7**) was recovered. A similar behavior was also observed to the *o*-dithiophenol complex **8**.

In a previous work[10] we investigated, by an ab initio computational approach employing the hybrid density functional B3LYP method, the role of the metal in stabilizing the elusive intermediate *p*-dithiobenzoquinone in **7**. Computational analyses using density functional theory confirm a net transfer of about 0.8 units of electron density to the π* ligand LUMO. 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. This provides further confirmation of the versatility of the "Cp*Ir" metal fragment in stabilizing reactive π systems. Having these thioquinoid complexes in hand for the first time, we investigated the reactivity of the *o*-thioquinoid metal complex [Cp*Ir-*o*-(η^4-$C_6H_4S_2$)] (**6**) towards electrophilic platinum adduct "(bpy)-$Pt(OTf)_2$".

When the *o*-dithiobenzoquinone metal complex [Cp*Ir-*o*-(η^4-$C_6H_4S_2$)] (**6**) was treated with [(bpy)$PtCl_2$] in CH_3CN in the presence AgOTf, a new compound was obtained, which was fully characterized as [Pt(bpy){Cp*Ir-*o*-(η^4-$C_6H_4S_2$)}][OTf]$_2$ (**10**) (see Experimental Section); further, the X-ray molecular structure of **10** was determined. The ^{1}H NMR of **10** recorded in CD_3CN shows the presence of two doublets of doublets at δ = 6.68 ppm and at δ = 7.07 ppm attributed to the metallated *o*-thioquinone and a singlet at δ = 1.98 ppm assigned to the Cp*Ir moiety. Further, we note the presence of four multiplets assigned to the "(bpy)Pt" fragment. Red crystals of **10** were obtained from nitromethane/ether solution. Complex **10** crystallizes in the monoclinic unit cell, space group $P2_1/c$. A view of the cationic part of the complex and selected bond lengths and angles are shown in Figure 3. The structure of **10** shows indeed that the *o*-thioquinone iridium complex chelates the "(bpy)Pt" fragment through the two sulfur centers such that the coordination geometry around the Pt becomes square planar. Because of this coordination mode, the aromatic ring of the *o*-thioquinone is planar and symmetrically bound (η^6-) to the Cp*Ir moiety.

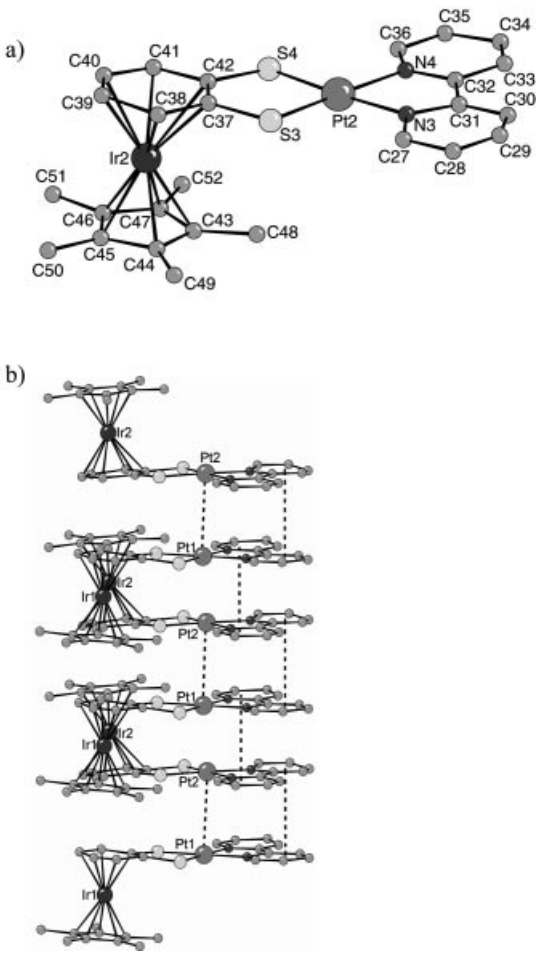


Figure 3. (a) View of the cationic part of complex **10**. Selected bond lengths [Å] and angles [°] for **10**: Ir2···C37 2.382(5), Ir2···C38 2.350(1), Ir2···C39 2.290(3), Ir2···C40 2.215(7), Ir2···C41 2.252(5), Ir2···C42 2.341(5), C42···S4 1.748(5), C37···S3 1.709(0), Pt2···S4 2.283(2), Pt2···S3 2.301(8), Pt2···N4 2.093(7), Pt2···N3 2.098(1), S4–Pt2–S3 89.51(1), S4–Pt2–N4 96.07(2), S3–Pt2–N3 94.99(2), N4–Pt2–N3 79.40(1). (b) 1D supramolecular chain formed through π–π and Pt···Pt contacts between individual molecules.

Further examination of the crystal packing of **10** reveals important information such as: the molecules are stacked in a head-to-tail orientation with several π–π interactions between adjacent bipyridyl ligands with d = 3.484 Å and d = 3.669 Å and also show the presence of a Pt1···Pt2 interaction at d = 3.574 Å. These Pt···Pt/π–π interactions occur in an alternate fashion among the individual molecules of [Pt(bpy){Cp*Ir-*o*-(η^4-$C_6H_4S_2$)}]$^{2+}$, describing a 1D supramolecular chain. In this supramolecular assembly each square planar Pt(bpy) subunit is rotated by 38.54° relative to the adjacent molecule. Other platinum(II) polypyridyl complexes have shown similar extended linear chain packing.[17] Our results, in which we describe the structure of a *o*-thioquinone metal complex for the first time and also its coordination chemistry, are unprecedented.

Concluding Remarks

In this paper we have reported the first synthesis and full characterization of *o*- and *p*-thiobenzoquinone metal complexes [Cp*Ir-*o*-(η^4-$C_6H_4S_2$)] (**6**) and [Cp*Ir-*p*-(η^4-$C_6H_4S_2$)] (**7**). The key molecules to their synthesis are the halogenated arene π complexes [Cp*Ir-*o*-(η^6-$C_6H_4Cl_2$)][BF_4]$_2$ (**4**) and [Cp*Ir-*p*-(η^6-$C_6H_4Cl_2$)][BF_4]$_2$ (**5**), which we prepared following a novel synthetic procedure. The structure of **7** was also reported and shows the "Cp*Ir" moiety is coordinated in a η^4-fashion to the *p*-thiobenzoquinone. This illustrates the role of the "Cp*Ir" fragment in stabilizing such reactive intermediates. The *o*-thiobenzoquinone iridium complex can be used as an *organometallic linker* and chelates the electrophilic "(bpy)$Pt(OTf)_2$" adduct, which provides a 1D supramolecular assembly [Pt(bpy){Cp*Ir-*o*-(η^4-$C_6H_4S_2$)}][OTf]$_2$ (**10**). Our future objectives are directed towards the use of these first thioquinoid complexes **6** and **7** as *organometallic linkers* in a similar way to the related benzoquinone metal complex[18] in order to construct novel supramolecular coordination polymers exhibiting short Pt···Pt contacts and also to study their photoluminescence properties.

Experimental Section

All experimental manipulations were carried out under argon using Schlenk tube techniques. The ^1H, ^{13}C, and ^{19}F NMR spectra were recorded in CD_2Cl_2, CD_3CN, and CD_3NO_2 using a Bruker Avance 400 NMR spectrometer at 400.13, 100.61, and 376.45 MHz, respectively. Infrared spectra were recorded from KBr discs on a Bio-Rad FTIR spectrometer FTS 165.

Synthesis of [Cp*Ir-*o*-(η^6-$C_6H_4Cl_2$)][BF_4]$_2$ (4): A solution of $AgCF_3SO_3$ (260 mg, 1.0 mmol) in acetone (10 mL) was added to [Cp*Ir(μ-Cl)Cl]$_2$ (200 mg, 0.25 mmol) in acetone (5 mL) to rapidly give a white precipitate of AgCl. The reaction mixture was stirred for 15 min then the resulting yellow solution of [Cp*Ir(acetone)$_3$][OTf]$_2$ (**3**) was filtered under argon into a dry Schlenk tube containing 1,2-dichlorobenzene (0.6 mL, 5.0 mmol) and the solvent was removed under vacuum. $BF_3{\cdot}2H_2O$ (1 mL) was added to the yellow residue, which immediately decolorized. The mixture was stirred for 30 min at room temperature, then diethyl ether (60 mL) was added. Complex **4** precipitated out as a white microcrystalline air-sensitive powder that was filtered and washed several times with diethyl ether (20 mL) and dried under vacuum (300 mg, 0.47 mmol). Yield: 94%. This complex is highly air- and moisture-sensitive and hence accurate elemental analysis could not be obtained. $C_{16}H_{19}B_2Cl_2F_8Ir$ (648 g mol^{-1}): calcd. C 29.65, H 2.96; found C 28.40, H 2.87. ^1H NMR (400 MHz, CD_3NO_2): δ = 2.35 (s, 15 H, Cp*), 7.52 (dd, 2 H, aromatic, $^3J_{H,H}$ = 4.7, $^4J_{H,H}$ = 2.7 Hz), 7.83 (dd, 2 H, aromatic, $^3J_{H,H}$ = 4.7, $^4J_{H,H}$ = 2.7 Hz) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_3NO_2): δ = 9.4 (s, –CH_3, Cp*), 109.3 (s, C=C, Cp*), 99.1 (s, C–H, aromatic), 100.3 (s, C–H, aromatic), 117.3 (s, C–Cl, aromatic) ppm. ^{19}F NMR (376 MHz, CD_3NO_2): δ = –152.7 (s, BF_4) ppm. IR (KBr disk): $\tilde{\nu}$(B–F) = 1083 cm^{-1}.

Synthesis of [Cp*Ir-*p*-(η^6-$C_6H_4Cl_2$)][BF_4]$_2$ (5): This complex was prepared in a similar way to that of [Cp*Ir-*o*-(η^6-$C_6H_4Cl_2$)][BF_4]$_2$ (**4**), using $AgCF_3SO_3$ (520 mg, 2 mmol), [Cp*Ir(μ-Cl)Cl]$_2$ (400 mg, 0.5 mmol) and $BF_3{\cdot}2H_2O$ (1 mL). Yield: 80% (515 mg, 0.8 mmol). This complex is highly air- and moisture-sensitive and hence accurate elemental analysis could not be obtained. $C_{16}H_{19}B_2Cl_2F_8Ir$ (648 g mol^{-1}): calcd. C 29.65, H 2.96; found C 27.39, H 2.96. ^1H NMR (400 MHz, CD_3NO_2): δ = 2.48 (s, 15 H, Cp*), 7.82 (s, 4 H, aromatic) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_3NO_2): δ = 8.3 (s, –CH_3, Cp*), 108.5 (s, C=C, Cp*), 99.4 (s, C–H, aromatic), 114.9 (s, C–Cl, aromatic) ppm. ^{19}F NMR (376 MHz, CD_3NO_2): δ = –153.6 (s, BF_4) ppm. IR (KBr disk): $\tilde{\nu}$(B–F) = 1083 cm^{-1}.

Synthesis of [Cp*Ir-*o*-(η^4-$C_6H_4S_2$)] (6): A solution of **3** (340 mg, 0.52 mmol) in CH_3CN (10 mL) was added to a suspension of dried HSNa (360 mg, 6.0 mmol) in CH_3CN (5 mL) and the mixture was stirred for 20 min at room temperature, then the solvent was removed by evaporation under vacuum. The residue was extracted by CH_2Cl_2 (20 mL) and filtered through Celite. After filtration through Celite, CH_2Cl_2 was evaporated under vacuum. Complex **6** was obtained as an orange microcrystalline powder (238 mg, 0.49 mmol). Yield: 88%. M.p. 185 °C (dec.) $C_{16}H_{19}IrS_2{\cdot}3H_2O$ (522 g mol^{-1}): calcd. C 36.73, H 4.30, S 12.39; found C 36.84, H 4.83, S 12.29. ^1H NMR (300 MHz, CD_2Cl_2): δ = 1.87 (s, 15 H, Cp*), 5.90 (dd, 2 H, diene, $^3J_{H,H}$ = 7.37, $^4J_{H,H}$ = 1.77 Hz), 6.44 (dd, 2 H, diene, $^3J_{H,H}$ = 7.37, $^4J_{H,H}$ = 1.77 Hz) ppm. IR (KBr disk): $\tilde{\nu}$(C=S) = 1085 cm^{-1}.

Synthesis of [Cp*Ir-*p*-(η^4-$C_6H_4S_2$)] (7): This complex was prepared in a similar way to that of Cp*Ir-*o*-(η^4-$C_6H_4S_2$)] (**6**), using HSNa (360 mg, 6.0 mmol) and **3** (340 mg, 0.52 mmol). Complex **7** was obtained as an orange microcrystalline powder (238 mg, 0.49 mmol). Yield: 95%. M.p. 160 °C (dec.) $C_{16}H_{19}IrS_2{\cdot}H_2O$ (486 g mol^{-1}): calcd. C 39.57, H 4.36, S 13.20; found C 38.96, H 4.32, S 13.24. ^1H NMR (400 MHz, CD_2Cl_2): δ = 1.91 (s, 15 H, Cp*), 5.96 (s, 4 H, aromatic) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ = 7.1 (s, –CH_3, Cp*), 96.25 (s, C=C, Cp*), 91.8 (s, C–H, aromatic), 148.1 (s, C=S, aromatic) ppm. IR (KBr disk): $\tilde{\nu}$(C=S) = 1096 cm^{-1}.

Synthesis of [Cp*Ir-*o*-(η^6-HS–C_6H_4-SH)][BF_4]$_2$ (8): $HBF_4{\cdot}Et_2O$ (1 mL) was added to a solution of [Cp*Ir-*o*-(η^4-$C_6H_4S_2$)] (50 mg, 0.1 mmol) in CH_3CN (3 mL), causing the purple solution to rapidly turn red. The reaction was left to proceed for 10 min. Addition of Et_2O (50 mL) provided a red oil-like substance (61 mg, 0.095 mmol). Yield: 95%. This compound is unstable, hence elemental analysis could not be performed. ^1H NMR (300 MHz, CD_3CN): δ = 2.10 (s, 15 H, Cp*), 6.83 (dd, 2 H, diene, $^3J_{H,H}$ = 7.37, $^4J_{H,H}$ = 1.77 Hz), 7.70 (dd, 2 H, diene, $^3J_{H,H}$ = 7.37, $^4J_{H,H}$ = 1.77 Hz) ppm. IR (KBr disk): $\tilde{\nu}$(B–F) = 1083 (s, br) cm^{-1}.

Synthesis of [Cp*Ir-*p*-(η^6-HS–C_6H_4-SH)][BF_4]$_2$ (9): This compound was prepared in a similar way to that of **8**. Complex **9** was obtained as a yellow microcrystalline substance. Yield: 93%. This compound is unstable, hence elemental analysis could not be performed. ^1H NMR (300 MHz, CD_3CN): δ = 1.98 (s, 15 H, Cp*), 7.15 (s, 4 H, diene) ppm. IR (KBr disk): $\tilde{\nu}$(B–F) = 1083 (s, br) cm^{-1}.

Synthesis of [Pt(bpy){Cp*Ir-*o*-(η^4-$C_6H_4S_2$)}][OTf]$_2$ (10): A solution of AgOTf (52 mg, 0.20 mmol) in CH_3CN (10 mL) was added to a suspension of [(bpy)$PtCl_2$][19] (42 mg, 0.10 mmol) in CH_3CN (10 mL) and the mixture was stirred for 4 h at room temperature and then filtered through Celite. [Cp*Ir-*o*-(η^4-$C_6H_4S_2$)] (53 mg, 0.11 mmol) in CH_3CN (10 mL) was added to the pale yellow filtrate solution (60 mL); after one hour at room temperature, the solvent was removed under vacuum and the orange powder obtained was washed twice with acetone (5 mL) and CH_2Cl_2 (5 mL). Complex **10** was obtained as an orange microcrystalline powder (101 mg, 0.09 mmol). Yield: 91%. $C_{28}H_{27}F_6IrN_2O_6PtS_4{\cdot}CH_2Cl_2$ (1200.95 g mol^{-1}): calcd. C 28.98, H 2.43, N 2.33, S 10.67; found C 28.96, H 2.33, N 2.45, S 11.32. ^1H NMR (300 MHz, CD_3CN): δ = 1.98 (s, 15 H, Cp*), 6.68 (dd, 2 H, aromatic, $^3J_{H,H}$ = 4.63, $^4J_{H,H}$ = 2.41 Hz), 7.07 (dd, 2 H, aromatic, $^3J_{H,H}$ = 4.63, $^4J_{H,H}$ = 2.41 Hz), 7.74 (ddd, 2 H, bpy, $^3J_{H,H}$ = 7.42 Hz, $^3J_{H,H}$ = 5.65, $^4J_{H,H}$ = 1.69 Hz), 8.34 (m, 2 H, bpy), 8.39 (m, 2 H, bpy), 8.84 (dd, bpy, 2 H, $^3J_{H,H}$ = 5.73, $^4J_{H,H}$ = 1.53, $^5J_{H,H}$ = 0.69 Hz) ppm. IR (KBr disk): $\tilde{\nu}$($CF_3SO_3^-$) = 1031; 1260 cm^{-1}.

X-ray Molecular Structures of 7 and 10: Suitable crystals of [Cp*Ir-*p*-(η^4-$C_6H_4S_2$)] (**7**) or [Pt(bpy){Cp*Ir-*o*-(η^4-$C_6H_4S_2$)}][OTf]$_2$ (**10**) were obtained using slow diffusion techniques from CH_2Cl_2/diethyl ether solution for **7** and from CH_3NO_2/diethyl ether for **10**. The selected crystal of the very moisture-sensitive **7** or **10** was rapidly selected, mounted onto a glass fiber, and transferred in a cold nitrogen gas stream. Orange crystals of **7**: $C_{48}H_{57}Ir_3S_6{\cdot}1/2CH_2Cl_2$, monoclinic, $P2_1/m$, a = 14.5450(5), b = 9.2730(11), c = 20.6380(3) Å, β = 94.271(4)°, V = 2775.8(5) Å^3, Z = 2, T = 250(2) K, μ = 7.476 mm^{-1}, 33263 reflections measured, 8342 independent (R_{int} = 0.0413), 6364 observed [$I \geq 2\sigma(I)$], 321 parameters, final R indices R_1 [$I \geq 2\sigma(I)$] = 0.0335 and wR_2 (all data) = 0.0956, gof on F^2 = 1.027, max./min. residual electron density = 1.31/–1.34 e Å^{-3}. Red crystals (**10**): $(C_{26}H_{27}IrN_2PtS_2)_2(CF_3O_3S)_4{\cdot}CH_3NO_2$, monoclinic, $P2_1/c$, a = 8.793(3), b = 34.296(9), c = 25.208(6) Å, β = 91.621(9)°, V = 7599(4) Å^3, Z = 4, T = 200(2) K, μ = 7.471 mm^{-1}, 65719 reflections measured, 22256 independent (R_{int} = 0.0615), 9023 observed [$I > 2\sigma(I)$], 848 parameters, final R indices R_1 [$I > 2\sigma(I)$] = 0.0832 and wR_2 (all data) = 0.1928, gof on F^2 = 1.033, max./min. residual electron density = 3.33/–3.29 e Å^{-3}. Intensity data were collected with a Bruker-Nonius Kappa-CCD with graphite-mono-

chromated Mo-K_α radiation. Unit-cell parameters determination, data collection strategy and integration were carried out with the Nonius EVAL-14 suite of programs.[20] The structures were solved by direct methods using the SHELXS-86 program[21] and refined anisotropically by full-matrix least-squares methods using the SHELXL-97 software package.[22]

CCDC-293581 (for **7**) and -620737 (for **10**) 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 also the footnote on the first page of this article): ^{1}H NMR spectra of complexes **4**, **5**, **8**, and **9** are included in the supplementary material.

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