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PREPARATION AND ELECTROCHEMICAL PROPERTIES OF PALLADIUM(0) COMPLEXES COORDINATED BY QUINONES AND 1,5-CYCLOOCTADIENE

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Summary

The complexes Pd(quinone)(COD) (COD = 1,5-cyclooctadiene) are prepared by a ligand substitution reaction of $Pd_2(DBA)_3$ (DBA = dibenzylideneacetone) in the presence of both quinone and COD. Palladium(0) complexes coordinated by quinones only are formed in the reaction in the absence of COD. The cyclic voltammetric behavior of Pd(quinone)(COD) has been studied. The reduction potentials for quinones shifted toward negative values on coordination to palladium(0). The oxidation potentials for the central palladium(0) in Pd(quinone)(COD) depend on the electron-withdrawing ability of the free quinones, and are in the following series: quinone = *p*-benzoquinone < 5,8-dihydro-1,4-naphthoquinone ~ 1,4-naphthoquinone < duroquinone. The shift of oxidation potentials for Pd(quinone)(COD) on changing the quinones as ligands is in contrast to that of Pd(quinone)(triphenylphosphine)$_2$.

Introduction

The complexes Ni(quinone)(COD) were prepared by a ligand substitution reaction of Ni(COD)$_2$, which can be handled easily, with quinones [1]. Pt(quinone)(COD)

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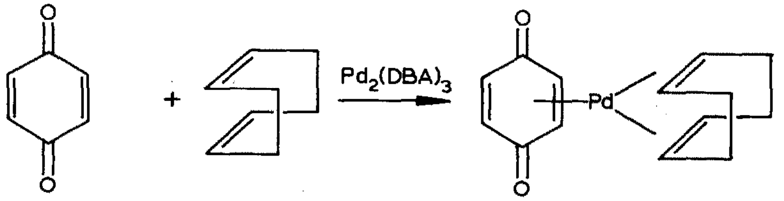
complexes were prepared similarly as a result of the development of a practical synthesis of $Pt(COD)_2$ [2,3]. However, Pd(quinone)(COD) complexes, have not yet been prepared, mainly because the handling of thermally unstable $Pd(COD)_2$ as a precursor is inconvenient. On the other hand, mixed olefin complexes of palladium(0) were prepared by a ligand substitution reaction of $Pd_2(DBA)_3(CHCl_3)$ or Pd_3(tribenzylideneacetylacetone)$_3(CHCl_3)$ with a judicious combination of both electron-donating olefins such as COD, and electron-withdrawing olefins such as maleic anhydride [4].

Previously, we reported the preparation of palladium(0) complexes containing a ligand which has both an electron-donating olefin site and an electron-withdrawing quinone or dihydro-quinone site in the ligand molecule [5]. In addition, we reported the electrochemical behavior of the free quinone derivatives and their complexes, Pd(quinone derivatives)$(PPh_3)_2$, from cyclic voltammetric measurement [6]. In this paper, we describe the preparation of Pd(quinone)(COD) complexes by a ligand substitution reaction of $Pd_2(DBA)_3(CHCl_3)$ with both quinones and COD. In addition, we report the cyclic voltammetric behavior of these complexes and compare the charge transfer in the case of Pd(quinone)(COD) with that in Pd(quinone)$(PPh_3)_2$.

Results and discussion

1.Preparation of Pd(quinone)(COD) complexes

The reaction of $Pd_2(DBA)_3(CHCl_3)$ with both *p*-benzoquinone (BQ) and COD in a 1/6/14 molar ratio in acetone under argon afforded Pd(BQ)(COD) in an 80% yield (eq.1). The reaction mixture gradually changed from a heterogeneous suspension to a homogeneous dark red solution. After the solution was filtered to remove the unchanged $Pd_2(DBA)_3(CHCl_3)$, diethyl ether was slowly added to the filtrate. The resulting dark brown crystals were filtered off, washed with cold acetone, then diethyl ether, and dried.



(1)

BQ COD

Similarly, the corresponding Pd(quinone)(COD) complexes were obtained by using 1,4-naphthoquinone (NQ), 5,8-dihydro-1,4-naphthoquinone (DHNQ), or duroquinone (DQ) instead of BQ. However, the corresponding Pd(quinone)(mono-ene) complex was not obtained by using a mono-ene such as cyclohexene. This is different than in the case of mixed olefin complexes of palladium(0) such as Pd(maleic anhydride)$_2$(cyclopentene) [4].

These complexes appear to be fairly stable in air in their solid states. They decomposed gradually in the usual organic solvents under an atmosphere of air to precipitate metallic palladium. They are soluble in acetone and chloroform, but only

TABLE 1

DECOMPOSITION POINTS AND ANALYTICAL DATA FOR Pd(QUINONE)(COD)

Pd(quinone)(COD)	Yield (%)	Decomp. (°C)	Analyses found (calcd.) (%)	
Quinone			C	H
p-Benzoquinone(BQ)	80	89–91	52.23 (52.10)	4.94 (5.01)
5,8-Dihydro-1,4-naphthoquinone (DHNQ)	49	61–63	57.84 (57.69)	5.51 (5.38)
1,4-Naphthoquinone (NQ)	55	72–74	58.22 (58.00)	5.15 (4.87)
Duroquinone (DQ)	48	111–113	57.03 (57.07)	6.52 (6.40)

slightly soluble in benzene and hexane. Table 1 summarizes the decomposition points and elemental analyses of the new Pd(quinone)(COD) complexes obtained.

2. *NMR and infrared spectra of the complexes*

In order to obtain information on the structure of the complexes, the ^{1}H NMR and the infrared spectra were measured in $CDCl_3$ and in $CHCl_3$, respectively. Table 2 presents the NMR and infrared data for Pd(quinone)(COD) in comparison with Pd(quinone)$(PPh_3)_2$. In the NMR spectra for Pd(quinone)(COD) complexes, upfield shifts of the conjugated olefinic proton signals (H(1)) of quinones were observed. The extent of the shifts (ΔH(1) = Free − Complexed) of the Pd(quinone)(COD) complex was smaller than that of Pd(quinone)$(PPh_3)_2$. This may indicate that PPh_3 is a stronger electron donor as a ligand in the palladium(0) complexes than is COD. This fact is in agreement with the result of electrochemistry of these complexes as described below.

Upfield shifts of the olefinic proton signals (CH, CH_2) of COD were also observed. When these shifts are compared with those of the conjugated olefinic proton signals of quinones, they are rather small in general (about 0.1 ~ 0.3 ppm). However, in the case of the duroquinone complex, Pd(DQ)(COD), an upfield shift of about 1.0 ppm of the olefinic proton signal for COD was observed.

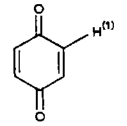
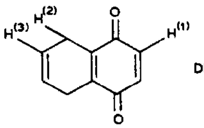
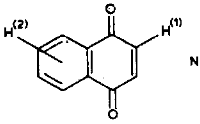
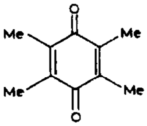
In the infrared spectra, the frequencies of the ν(C=O) band of the quinones were decreased by 40–80 cm^{-1} on coordination to palladium(0). The lowering of ν(C=O) in Pd(DQ)(COD) was the largest (about 80 cm^{-1}) among the four complexes, but it was quite small compared with the case of [Mo(acrolein)$_2$(CO)$_2$], where the ν(CO) value of acrolein bound to the metal atom through both the C=C and C=O groups is decreased by 150 cm^{-1} [7]. This would indicate that there is no or only weak interaction between the C=O group and palladium(0) in Pd(DQ)(COD).

3. *Ligand exchange reaction*

In order to determine the relative stabilities of Pd(quinone)(COD) and Pd(quinone)$(PPh_3)_2$, a ligand exchange reaction was investigated. Pd(BQ)(COD) reacted with triphenylphosphine in a 1/2 molar ratio in chloroform at room

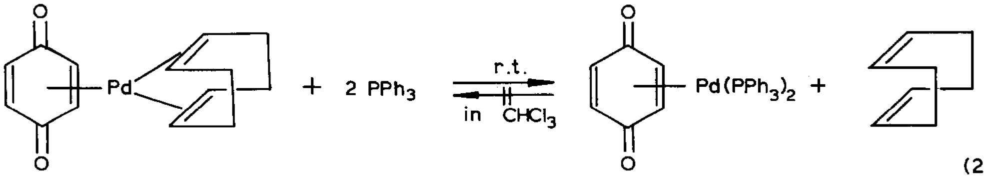
TABLE 2

^{1}H NMR AND IR DATA FOR FREE OR COMPLEXED QUINONES AND COD WITH PALLADIUM(0)

Pd(quinone)(COD)	Proton assign. [a]	δ(ppm) (in $CDCl_3$)		ν(C=O) (cm^{-1}) [c]	
quinone		Free	Complexed [b]	Free	Complexed [b]
 BQ	$H^{(1)}$	6.80	5.83(5.33)		1613
	CH	5.54	5.44	1656	
	CH_2	2.39	2.42		(1620)
 DHNQ	$H^{(1)}$	6.71	5.38(4.60)		
	$H^{(2)}$	3.06	3.10(2.65)		1600
	$H^{(3)}$	5.80	5.85(5.71)	1653	
	CH	5.54	5.21		(1612)
	CH_2	2.39	2.38		
 NQ	$H^{(1)}$	6.97	5.03(4.67)		
	$H^{(2)}$	7.7–8.2	7.5–8.2(7.3–7.6)		1623
	CH	5.54	5.37	1670	
	CH_2	2.39	2.22		(1629)
 DQ	Me	2.01	2.14		
	CH	5.54	4.57	1643	1564
	CH_2	2.39	2.36		

[a] Both CH and CH_2 are assigned to COD. [b] The values in the parentheses correspond to $Pd(quinones)(PPh_3)_2$. [c] In $CHCl_3$.

temperature under argon to give $Pd(BQ)(PPh_3)_2$ and free COD (eq.2). It was also confirmed that no reverse reaction occurred. This fact demonstrates that $Pd(BQ)(PPh_3)_2$ is more stable than Pd(BQ)(COD).

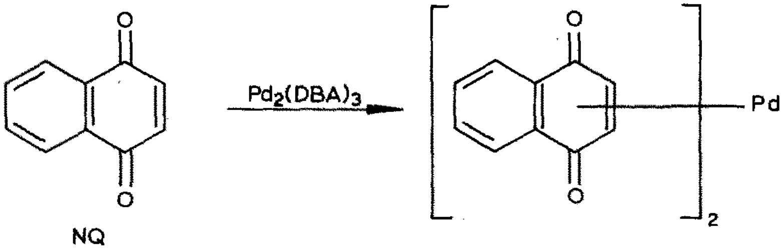


(2)

4.Preparation of palladium(0) complexes coordinated by quinones only

Palladium(0) complexes coordinated by quinones only were obtained from the reaction of $Pd_2(DBA)_3(CHCl_3)$ with quinones in the absence of COD. $Pd_2(DBA)_3(CHCl_3)$ reacted with excess of BQ in acetone over a period of 100 min under argon to afford an insoluble complex, $Pd(BQ)_x$ ($x \doteqdot 1$), in the usual solvents. In the infrared spectrum, the frequency of the ν(C=O) band of BQ was decreased by 22 cm^{-1} on coordination to palladium(0). The $Pd(BQ)_x$ may have a polymeric structure similar to that of $Ni(DQ)_x$ ($x \doteqdot 1$) reported [8].

The reaction of $Pd_2(DBA)_3(CHCl_3)$ with NQ under similar conditions gradually afforded $Pd(NQ)_2$ as a yellow-brown precipitate in a 95% yield (eq.3).



NQ

(3)

Table 3 summarizes elemental analyses, NMR and infrared data for $Pd(NQ)_2$. In the ^1H NMR spectrum of $Pd(NQ)_2$, upfield shifts of the conjugated olefinic proton signal of NQ were observed. In the infrared spectrum, the frequency of the ν(C=O) band of NQ was decreased by 60 cm^{-1} on coordination to palladium(0). $Pd(NQ)_2$ was more soluble in the usual solvents than was $Pd(BQ)_x$. Therefore, presumably the $Pd(NQ)_2$ does not have a polymeric structure similar to that of $Pd(BQ)_x$, though evidence for the monomeric form of the $Pd(NQ)_2$ was not obtained. When using DQ, $Pd_2(DBA)_3(CHCl_3)$ was recovered unchanged after 100 min at room temperature.

5. The electrochemistry of Pd(quinone)(COD) complexes

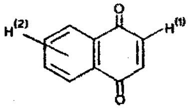
The electrochemical behavior of Pd(quinone)(COD) was complicated by the phenomenon of dissociation in a dilute solution. The Pd(quinone)(COD) complexes were more subject to dissociation than was $Pd(quinone)(PPh_3)_2$. The dissociation of Pd(quinone)(COD) was observed even in acetonitrile, which was a suitable solvent for measurements of the cyclic voltammograms (CV) of $Pd(quinone)(PPh_3)_2$. Presumably, ligand exchange reaction occurs among Pd(BQ)(COD) and a large excess of acetonitrile as solvent to liberate free COD, because the proton signals not of free *p*-benzoquinone but of free COD were observed in NMR spectra in CD_3CN. So the CV for Pd(quinone)(COD) were measured in acetone, after it was confirmed by NMR measurements that both quinones and COD do coordinate to palladium(0) in deuterated acetone. The CV for $Pd(quinone)(PPh_3)_2$ were also measured under similar conditions for comparison.

The CV for Pd(BQ)(COD) is shown as an example in Fig. 1, together with those for BQ, $Pd(PPh_3)_4$, and $Pd(BQ)(PPh_3)_2$ for comparison. The CV in acetone was not better-defined than the CV in acetonitrile. In particular, the reduction peak (a) corresponding to BQ coordinated to palladium(0) was not observed clearly. On the other hand, the oxidation peak (b) was well-defined. The corresponding reoxidation and rereduction peaks were illdefined, showing the irreversibility of the electrode reactions. Tentative schemes for electrode reaction may be explained similarly to those of $Pd(quinone)(PPh_3)_2$ reported [6] (Schemes 1 and 2).

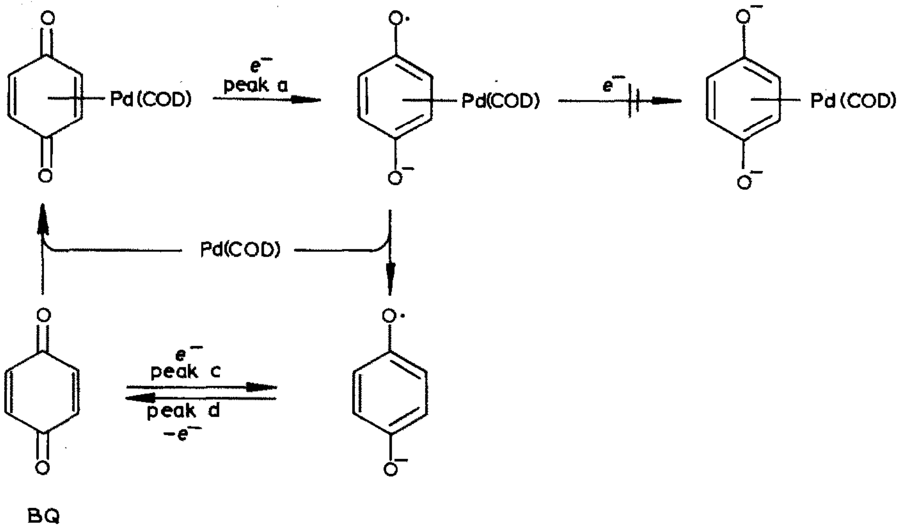
Table 4 shows the reduction peak potentials for the complexed quinones, the oxidation peak potentials for the central palladium(0) of Pd(quinone)(COD), and those of $Pd(quinone)(PPh_3)_2$ as a reference. The reduction peak potentials for the complexed quinones of Pd(quinone)(COD) showed a similar tendency to those of $Pd(quinone)(PPh_3)_2$. That is, the shifts of reduction potentials for quinones, $|\Delta E|$, caused by the coordination to palladium(0), indicated a similar dependence on the

TABLE 3

DECOMPOSITION POINT, ANALYTICAL DATA, ^{1}H NMR AND IR DATA FOR Pd(NQ)$_2$

Pd(NQ)$_2$ / NQ	Yield (%)	Decomp. (°C)	Analyses found (calcd.) (%)		Proton assign.	δ(ppm) (in DMSO-d_6)		ν(CO) (cm^{-1}) (KBr)	
			C	H		Free	Compl.	Free	Compl.
	95	95–99	56.94	2.67	H$^{(1)}$	7.13	6.79	1645	1586
			(56.83)	(2.86)	H$^{(2)}$	8.0	8.0		

SCHEME 1



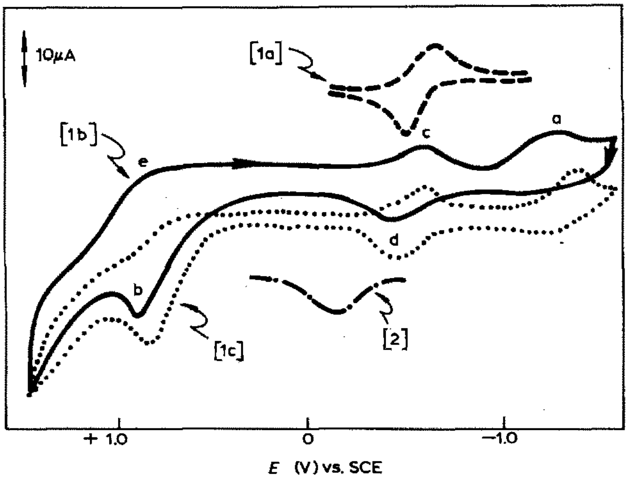
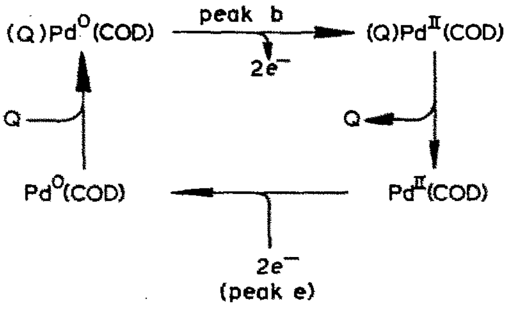


Fig. 1. Cyclic voltammograms of (*p*-benzoquinone)Pd(COD) (**1b**), *p*-benzoquinone (**1a**), Pd(PPh$_3$)$_4$ (**2**) and (*p*-benzoquinone)Pd(PPh$_3$)$_2$ (**1c**) Conc. 10^{-3} *M* for **1a**, **1b** and **1c**; 10^{-4} *M* for **2** Scan rate: 100 mV/sec, 0.1 *M* NEt$_4$PF$_6$-(CH$_3$)$_2$CO at 25°C.

SCHEME 2



electron-withdrawing ability of the free quinones except for DQ. However, the oxidation peak potentials for the central palladium(0) of Pd(quinone)(COD) showed a different tendency from those of Pd(quinone)(PPh_3)$_2$. The oxidation peak potentials for the central palladium(0) of Pd(quinone)(PPh_3)$_2$ scarcely depended on the electron-withdrawing ability of the free quinones, but those of Pd(quinone)(COD) did depend on it. This fact may show that the COD ligand can scarcely compensate the outflow of electron density from palladium(0) to the quinone ligand. To sum up, it indicates that PPh_3 is more effective as an electron donating ligand than COD is.

Experimental

Apparatus

The infrared spectra were recorded on a Jasco IRA-1 spectrometer. The ^{1}H NMR spectra were measured on Hitachi-Perkin-Elmer R24 and R600 spectrometers. The ^{1}H NMR signals are referred to internal tetramethylsilane. The cyclic voltammograms were recorded on a Yanagimoto P-1000 voltammetric analyzer, X-Y recorder WX4401, and function generator FG-121B.

Chemicals and solvents

BQ and NQ were commercially available and were purified by recrystallization or sublimation. DQ and COD were used without purification. Free DHNQ and

TABLE 4

REDOX POTENTIALS FOR Pd(QUINONE)(COD)^{c,e}

Quinone		BQ	DHNQ	NQ	DQ
Free^{a}	$E^1(1/2)$ (V)^{b}	−0.46	−0.63	−0.69	−0.80
Complex^{a}	E_p(red) (V)	−1.19	−1.29	−1.33	< −1.70
		(−1.27)	(−1.27)	(−1.35)	–
	E_p(ox) (V)	0.94	0.85	0.83	0.71
		(0.88)	(0.86)	(0.88)	–
	$\|\Delta E\|^{d}$	0.73	0.66	0.64	> 0.90
		(0.81)	(0.64)	(0.66)	–

^{a} Scan rate = 0.1 V/sec. ^{b} Half-wave potentials for quinones. ^{c} Reference electrode: saturated calomel electrode (SCE). ^{d} $|\Delta E| = |E_p(\text{red}) \text{ for complex} - E^1(1/2) \text{ for free ligand}|$. ^{e} Data for Pd(quinones)(PPh_3)$_2$ were shown in parentheses.

$Pd(DHNQ)(PPh_3)_2$ were prepared by the literature method [5]. $Pd_2(DBA)_3(CHCl_3)$, $Pd(PPh_3)_4$, $Pd(BQ)(PPh_3)_2$, and $Pd(NQ)(PPh_3)_2$ were also prepared by reported methods [9–11]. Tetraethylammonium hexafluorophosphate (NEt_4PF_6) as supporting electrolyte was prepared by the literature method [12].

The solvents for electrochemical studies were purified before use. Acetonitrile was dried over calcium hydride, then over phosphorus pentoxide, and distilled repeatedly [13]. Acetone was dried over calcium chloride, then over phosphorus pentoxide, and distilled repeatedly [14].

Preparation of Pd(BQ)(COD)

BQ (314 mg, 2.91 mmol), COD (667 mg, 6.18 mmol), and $Pd_2(DBA)_3(CHCl_3)$ (467 mg, 0.452 mmol) were dissolved in acetone (10 ml) under argon at room temperature. The mixture was stirred for 1 h at room temperature, and gradually changed from a heterogeneous suspension to a homogeneous dark red solution. After the solution was filtered to remove the unchanged $Pd_2(DBA)_3(CHCl_3)$, diethyl ether (10 ml) was slowly added to the filtrate. The resulting dark brown crystals were filtered, washed with cold acetone (3 ml), then diethyl ether (12 ml), and dried in vacuo to yield crystals of Pd(BQ)(COD) (233 mg, 80% yield).

Preparation of Pd(DHNQ)(COD)

Similarly to the case of Pd(BQ)(COD), a mixture of DHNQ (744 mg, 4.65 mmol), COD (1.03 g, 9.54 mmol), and $Pd_2(DBA)_3(CHCl_3)$ (637 mg, 0.616 mmol) was stirred to yield yellow-red crystals of Pd(DHNQ)(COD) (226 mg, 49% yield).

Preparation of Pd(NQ)(COD)

Similarly to the case of Pd(BQ)(COD), a mixture of NQ (356 mg, 2.25 mmol), COD (466 mg, 4.31 mmol), and $Pd_2(DBA)_3(CHCl_3)$ (605 mg, 0.585 mmol) was stirred to yield red crystals of Pd(NQ)(COD) (240 mg, 55% yield).

Preparation of Pd(DQ)(COD)

Similarly to the case of Pd(BQ)(COD), a mixture of DQ (502 mg, 3.06 mmol), COD (398 mg, 3.69 mmol), and $Pd_2(DBA)_3(CHCl_3)$ (848 mg, 0.820 mmol) was stirred to yield yellow-brown crystals of Pd(DQ)(COD) (298 mg, 48% yield).

Ligand exchange reaction of Pd(BQ)(COD) with triphenylphosphine

To a solution of Pd(BQ)(COD) (65.0 mg, 0.202 mmol) in chloroform (5 ml), triphenylphosphine (106 mg, 0.404 mmol) in chloroform (5 ml) was added at room temperature and the mixture was stirred for 10 min. After removal of the solvent, the resulting red-brown solid was washed with hexane (20 ml), and dried in vacuo to yield $Pd(BQ)(PPh_3)_2$ quantitatively.

Preparation of $Pd(NQ)_2$

NQ (1.62 g, 10.3 mmol) and $Pd_2(DBA)_3(CHCl_3)$ (484 mg, 0.468 mmol) were dissolved in acetone (10 ml) under argon at room temperature. The mixture was stirred for 100 min at room temperature. As $Pd_2(DBA)_3(CHCl_3)$ dissolved with time, a yellow-brown powder gradually precipitated. The powder was filtered off, washed with cold acetone (5 ml), then with diethyl ether (15 ml), and dried in vacuo to yield a powder of $Pd(NQ)_2$ (377 mg, 95% yield).

Electrochemistry

Unless otherwise stated, the experiments were performed in acetone at a temperature of 25(± 1)°C under a nitrogen atmosphere. The concentration of the supporting electrolyte was 0.1 *M* and that of the electroactive species was 10^{-3} *M*. The working electrode was the stationary platinum electrode. An aqueous saturated calomel electrode (SCE) was used as the reference electrode (the experimental errors were ±0.01 V). The scan rate was 100 mV/s.

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