



# Isolation of *p*-tricyanovinylphenyldicyanomethide ion via a [2+2] cycloaddition of 7,7,8,8-tetracyanoquinodimethane (TCNQ) molecules

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## ABSTRACT

In the presence of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and dppm (bis(diphenylphosphino) methane), the reaction of TCNQ (7,7,8,8-tetracyanoquinodimethane) molecules by [2+2] cycloaddition forms a *p*-tricyanovinylphenyldicyanomethide ion ( $\text{PCQ}^-$ ), which has been obtained as one anion unit in one new compound  $[\text{Co}(\text{dppmdo})_3][\text{PCQ}^-]_2 \cdot \text{H}_2\text{O}$  **1** (dppmdo = bis(diphenylphosphine oxide) methane). Its structure was determined by X-ray crystallography: **1** crystallizes in  $P\bar{1}$  with  $a = 14.174(3)$  Å,  $b = 19.553(4)$  Å,  $c = 19.776(4)$  Å,  $\alpha = 112.72(3)^\circ$ ,  $\beta = 95.43(3)^\circ$ ,  $\gamma = 110.79(3)^\circ$ , and  $Z = 2$ . It was characterized by IR spectra, UV–Vis spectra, and cyclic voltammogram. Magnetic properties indicate that no magnetic coupling between  $\text{PCQ}^-$  and  $[\text{Co}(\text{dppmdo})_3]^{2+}$  unit.

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## 1. Introduction

The TCNQ molecule is the least ‘innocent’ ligand in coordination chemistry [1] due to its low-lying  $\pi^*$  orbital. Typically, this easily reducible compounds form radical ion  $\text{TCNQ}^-$  in its reactions with metal complexes, leading to mono-, di-, tri- or tetranuclear nitrile-bonded  $\sigma$  compounds, to  $\pi$  compounds with side-on coordination, or to corresponding ion pair compounds without direct coordination. Due to its powerful electron-accepting properties, TCNQ forms intermolecular charge-transfer (CT) complexes with various organic and inorganic electron donors, some of them exhibiting high electric conductivity or interesting magnetic behavior [2–19]. These properties make TCNQ still an attractive subject of contemporary advanced material research.

However, while the reactivity of TCNQ has been explored [20,21], some of the structural features of this molecule have obviously been ignored. Namely, it possesses two types of strongly electrondeficient CC double bonds that could, in analogy to tetracyanoethylene (TCNE) [22,23] undergo thermal [2+2] cycloaddition with electron-rich alkynes. Here, we describe such one reaction between TCNQ molecules, giving access to one polycyano ion  $\text{PCQ}^-$ .

## 2. Results and discussion

### 2.1. Synthesis and general properties

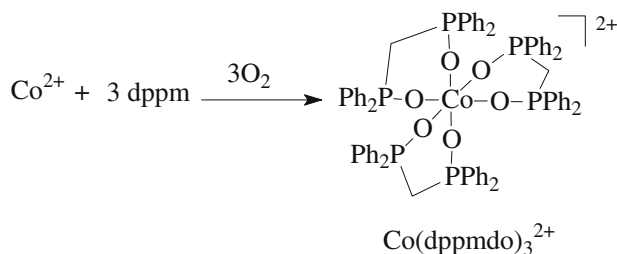
Considering the typically similar reactivity of the TCNQ molecule with paramagnetic transition metal centers (such as  $\text{Co}^{2+}$ ), the reaction of TCNQ ligand,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and dppm in methanol provided an unexpectedly different result.

Under air, the reaction of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and dppm provided high spin  $\text{Co}^{\text{II}}$  complex  $[\text{Co}(\text{dppmdo})_3]^{2+}$  (Scheme 1), and two TCNQ molecules react by [2+2] cycloaddition give a polycyano unit  $\text{PCQ}^-$ . The possible mechanism of the formation of polycyano ion  $\text{PCQ}^-$  is illustrated in Scheme 2. Treatment of TCNQ with  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , and dppm was anticipated to result in the formation of one  $\text{TCNQ}^-$  anion **A**, and complex  $[\text{Co}^{\text{III}}(\text{dppmdo})_3]^{3+}$ . The [2+2] cycloaddition reaction between the exocyclic CC double bond of  $\text{TCNQ}^-$  anions gave one cross-coupling intermediate **B**, which, in turn, rearranges to provide a  $\sigma/\sigma$  bonded  $(\text{TCNQ}_2)^{2-}$  **C** [24], followed by losing a dicyanomethyl-benzene radical to give one radical anion **D**. Furthermore, losing a cyanide radical to provide one charge-transfer compound **E** [25], which transfers charge from polycyano ion to cobalt complex  $[\text{Co}^{\text{III}}(\text{dppmdo})_3]^{3+}$  to give the observed product containing two  $\text{PCQ}^-$  ions and one complex  $[\text{Co}^{\text{II}}(\text{dppmdo})_3]^{2+}$  unit.

Infrared spectra of **1** show two main bands in the region of the cyanide stretching vibrations (Supplementary material). These bands situated between  $2177$  and  $2156 \text{ cm}^{-1}$  are shifted to lower energies relative to  $\nu(\text{CN}) > 2228 \text{ cm}^{-1}$  of the free TCNQ [26] but to higher energies relative to  $\nu(\text{CN})$  of TCNE [27]. It is also

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Scheme 1.

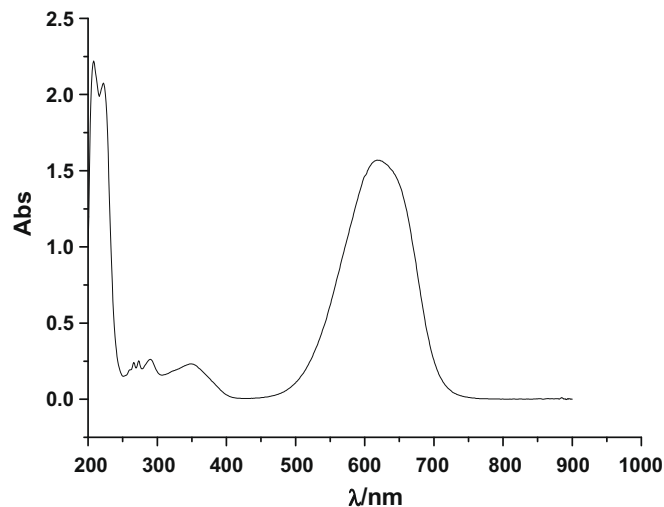
noteworthy that one sharp feature that appear at  $1161 \text{ cm}^{-1}$  is assigned to the stretching of P–O mode.

The absorption spectrum of compound **1** is shown in Fig. 1, one long wavelength absorption band at 620 nm can be attributed to an intra-ligand transition of polycyano ion  $\text{PCQ}^-$ . Compared with the spectra of the free ligand, the absorption band for **1** is blue-shifted for 23 nm, indicating there is charge transition between Co complex and  $\text{PCQ}^-$  [28].

## 2.2. Structure of compound 1

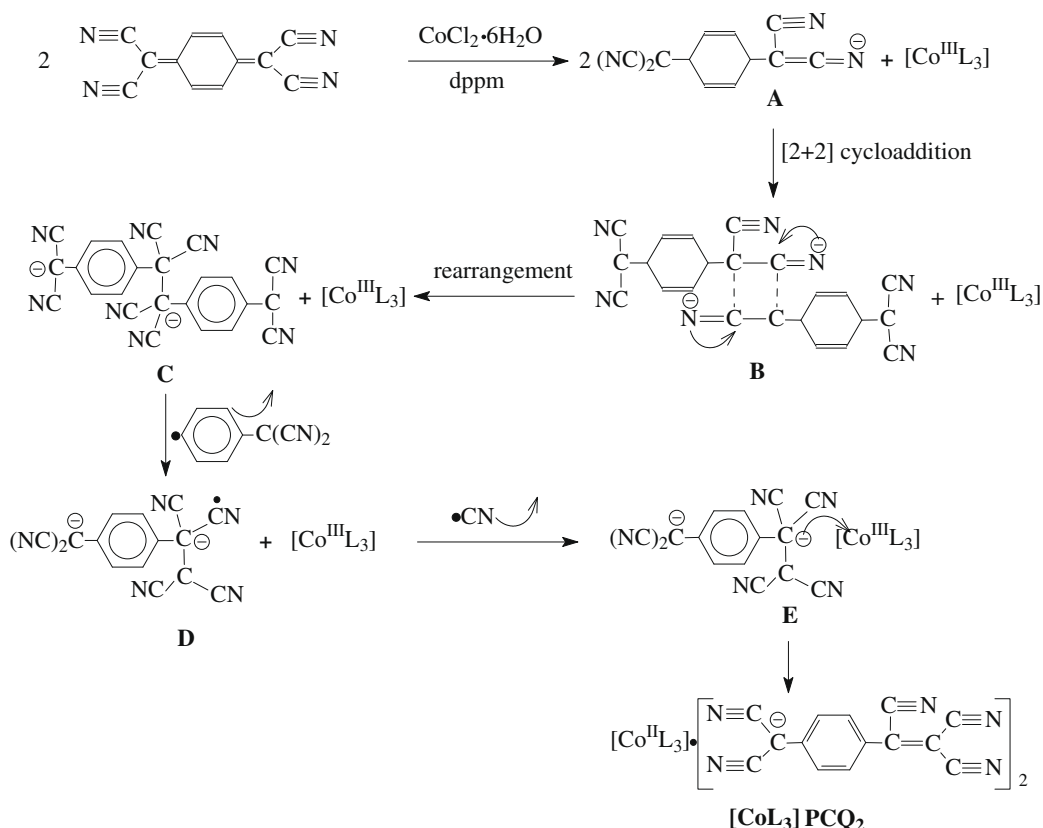
The compound **1** crystallizes in space group  $P\bar{1}$ , with two formula units present per unit cell. Table lists details of the crystal parameters, data collection and refinement for compound **1**. The selected bond distances and angles were listed in Table 2.

As shown in Fig. 2, the structure consists a cationic cobalt complex with a single  $\text{Co}^{2+}$  ion with octahedral geometry chelated by three dppmdo ligands,  $[\text{Co}(\text{dppmdo})_3]^{2+}$ , two polycyano anions and one  $\text{H}_2\text{O}$  molecule.

Fig. 1. Absorption spectrum of **1** in  $\text{CH}_3\text{CN}$ .

For polycyano ion  $\text{PCQ}^-$ , the  $\text{C}\equiv\text{N}$  distances show significant changes. The  $\text{C}\equiv\text{N}$  distances for tricyanovinyl group range from 1.129(8) to 1.150(9) Å, and the average  $\text{C}\equiv\text{N}$  distance for dicyanomethide group is 1.147(7) Å. In tricyanovinyl group, the average C–CN distance of 1.451(10) Å is 0.016 Å longer than that observed for the free TCNE (1.435 Å), the  $\text{NC}-\text{C}-\text{CN}$  bond angles of  $115.4(5)^\circ$  and  $121.9(7)^\circ$  are similar to the observed  $\text{NC}-\text{C}-\text{CN}$  angles of the free TCNE ( $116.5(12)^\circ$ ) in accord with its  $\text{sp}^2$  central carbon atom [29].

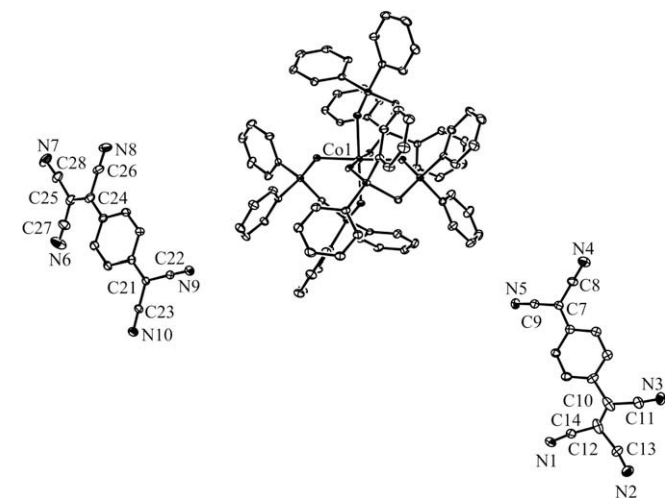
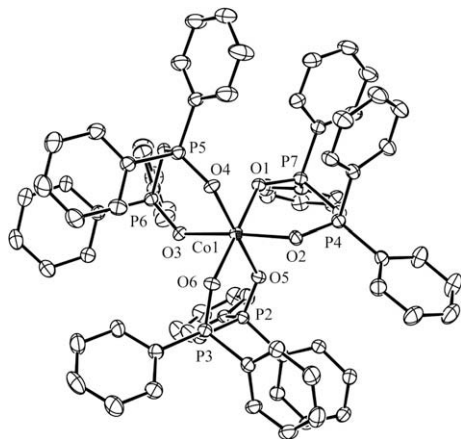
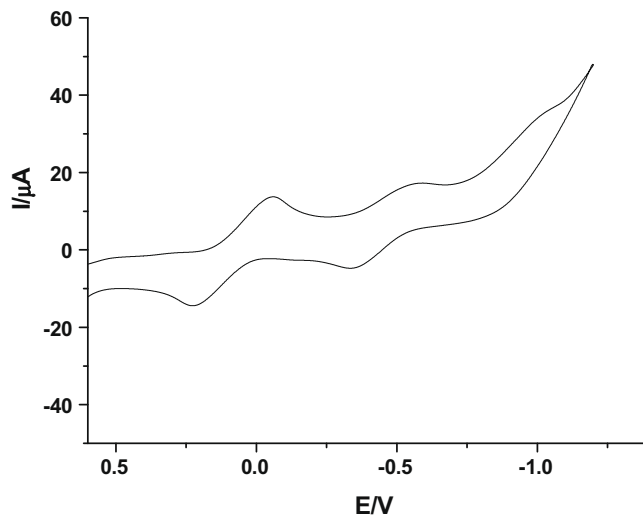
For Co complex unit (Fig. 3), the cobalt atom is surrounded nearly octahedral by six oxygen atoms from dppmdo ligands. The Co–O distances range from 2.077(3) to 2.157(3) Å.



Scheme 2. Reaction design.

**Table 1**  
Crystallographic data for **1**.

Empirical formula	C <sub>103</sub> H <sub>74</sub> CoN <sub>10</sub> O <sub>7</sub> P <sub>6</sub>
Formula weight	1808.47
$\lambda$ (Å)	0.71073
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> (Å)	14.174(3)
<i>b</i> (Å)	19.553(4)
<i>c</i> (Å)	19.776(4)
$\alpha$ (°)	112.72(3)
$\beta$ (°)	95.43(3)
$\gamma$ (°)	110.79(3)
<i>V</i> (Å <sup>3</sup> )	4552.4(16)
<i>Z</i>	2
<i>D<sub>c</sub></i> (M gm <sup>-3</sup> )	1.319
<i>F</i> (0 0 0)	1870
$\theta$ Range for data collection (°)	3.00–27.46
Reflections collected/unique	20 512/8519
Data/restraints/parameters	8519/0/1145
Goodness-of-fit (GOF) on <i>F</i> <sup>2</sup>	0.992
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0627, <i>wR</i> <sub>2</sub> = 0.1491
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.1775, <i>wR</i> <sub>2</sub> = 0.2086

**Fig. 2.** The ORTEP view of [Co(dppmdo)<sub>3</sub>][PCQ<sup>-</sup>]<sub>2</sub>·2H<sub>2</sub>O **1**. H<sub>2</sub>O molecule was omitted for clarity.**Fig. 3.** The ORTEP view of [Co(dppmdo)<sub>3</sub>]<sup>2+</sup> cation of **1**.**Fig. 4.** Cyclic voltammogram of **1** in CH<sub>3</sub>CN/0.1 M [Bu<sub>4</sub>N]ClO<sub>4</sub> at 100 mV s<sup>-1</sup> scan rate.**Scheme 3.**

### 2.3. Electrochemical properties

The electrochemical property of compound **1** was measured by cyclic voltammetry in CH<sub>3</sub>CN (Fig. 4). The free TCNQ molecule undergoes two reversible one-electron reduction at –0.651 and –0.05 V vs. AgCl/Ag in CH<sub>3</sub>CN [[1,30], Supplementary material], which is in accord with reversibly reduced in two steps. The compound **1** exhibits two much more anodically shifted one-electron reduction at –0.459 and 0.09 V vs. AgCl/Ag (Scheme 3), indicating that it is easier to reduce for PCQ than the free TCNQ molecule.

### 2.4. Magnetic property

The magnetic property of compound **1** is investigated in the temperature range 2–300 K for molar susceptibility. The magnetic behavior of **1** is shown in Fig. 5 in the form of  $\chi_{\text{M}}T$  vs. *T*. The value of  $\chi_{\text{M}}T$  at room temperature, 1.876 cm<sup>3</sup> K mol<sup>-1</sup> (3.88  $\mu_{\text{B}}$ ), is close to the value of high spin Co<sup>2+</sup> (*S* = 3/2) and keeps constant with decreasing temperature, indicating no magnetic coupling between PCQ<sup>-</sup> and [Co(dppmdo)<sub>3</sub>]<sup>2+</sup> unit.

## 3. Experimental

CoCl<sub>2</sub>·6H<sub>2</sub>O, dppm, and TCNQ were purchased from commercial sources and used as received.

### 3.1. Physical measurements

Infrared spectrum was recorded (in the 4000–400 cm<sup>-1</sup>) as KBr disks on a Bruker 1600 FTIR spectrometer. Electronic spectra were recorded on a Hitachi U-3010 (UV–Vis) spectrophotometer for the solution in CH<sub>3</sub>CN. <sup>31</sup>P NMR spectra were measured on a Bruker AM 500 spectrometer in DMF solution, Chemical shifts are quoted to 85% H<sub>3</sub>PO<sub>4</sub>. Magnetic susceptibility data for powder sample were collected in the temperature range 2–300 K with a Quantum

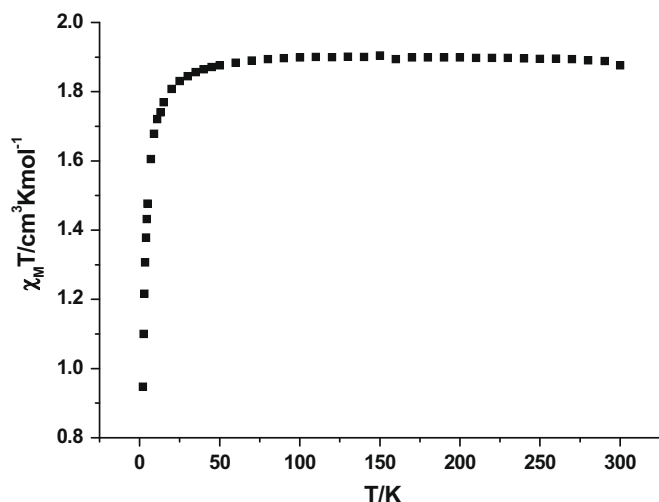


Fig. 5. Temperature dependence of  $\chi_M T$  at an applied magnetic field of 2000 Oe.

Table 2

Selected bond distances (Å) and angles (°) for compound **1**.

Bond distances (Å)			
Co(1)–O(4)	2.077(3)	Co(1)–O(5)	2.093(3)
Co(1)–O(2)	2.107(3)	Co(1)–O(3)	2.125(3)
Co(1)–O(6)	2.135(3)	Co(1)–O(1)	2.157(3)
C(25)–C(24)	1.353(9)	C(25)–C(27)	1.425(12)
C(25)–C(28)	1.438(9)	C(24)–C(26)	1.491(10)
C(24)–C(18)	1.424(8)	C(21)–C(22)	1.425(8)
C(21)–C(23)	1.391(7)	C(21)–C(15)	1.394(7)
C(27)–N(6)	1.137(12)	C(28)–N(7)	1.129(8)
C(26)–N(8)	1.150(9)	C(22)–N(9)	1.145(7)
C(23)–N(10)	1.149(7)		
Bond angles (°)			
C(27)–C(25)–C(28)	116.3(8)	C(28)–C(25)–C(24)	121.7(9)
C(27)–C(25)–C(24)	121.9(7)	C(25)–C(24)–C(26)	112.4(7)
C(18)–C(24)–C(25)	130.6(7)	C(18)–C(24)–C(26)	117.0(7)
C(15)–C(21)–C(22)	121.0(5)	C(15)–C(21)–C(23)	123.6(5)
C(22)–C(21)–C(23)	115.4(5)	N(6)–C(27)–C(25)	74.2(10)
N(7)–C(28)–C(25)	175.4(10)	N(8)–C(26)–C(24)	179.1(9)
N(9)–C(22)–C(21)	177.5(7)	N(10)–C(23)–C(21)	178.6(6)

Symmetry transformations used to generate equivalent atoms: #1  $x, y, z$ ; #2  $-x, -y, -z$ .

Design SQUID Magnetometer MPMS XL-7. Effective magnetic moments were calculated by the equation  $\mu_{\text{eff}} = 2.828(\chi_M T)^{1/2}$ , where  $\chi_M$  is the molar magnetic susceptibility. Electrochemical experiments were carried out with an Auto Lab instrument with a Platinum wire working electrode, a platinum plate counter electrode, and an AgCl/Ag electrode as the reference electrode. For the experiments performed in  $\text{CH}_3\text{CN}$  as solvent (ca.  $1.5 \times 10^{-5} \text{ mol L}^{-1}$ ) containing in  $0.1 \text{ mol L}^{-1}$  tetra-*n*-butylammonium perchlorate (TBAP) as supporting electrolyte, the potentials were referenced to an AgCl/Ag electrode.

### 3.2. Synthesis of compound **1**

All synthetic procedures were performed anaerobically. A solution of TCNQ (0.409 g, 2 mmol) in dichloromethane (10 mL), was added to a stirred solution of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.238 g, 1 mmol) and dppm (1.161 g, 3.02 mmol) in  $\text{CH}_3\text{CH}_2\text{OH}/\text{CH}_2\text{Cl}_2$  (1:1, 20 mL). The resulting solution was stirred for 2.5 h and filtered. Slow evaporation of the filtrate formed blue–green crystals, collected by filtration, and dried *in vacuo* (0.528 g, 29.5%). Anal. Calc. for  $\text{C}_{103}\text{H}_{72}\text{CoN}_{10}\text{O}_6\text{P}_6$ : C, 69.03; H, 4.02; N, 7.82. Found: C, 69.15; H, 4.01; N, 7.83%. IR bands (KBr pellets,  $\text{cm}^{-1}$ ):  $\nu = 3055$  (w), 2941

(w), 2883 (w) ( $\nu(-\text{Ph})$ );  $\nu = 2177$  (s), 2156 (m) ( $\nu(\text{C}\equiv\text{N})$ );  $\nu = 1161$  (s) ( $\nu(\text{P}-\text{O})$ );  $[\text{CH}_3\text{CN}, \lambda_{\text{max}}/\text{nm} (\epsilon/\text{L mol}^{-1} \text{ cm}^{-1})]$ : 620 ( $3.5 \times 10^4$ ), 347 ( $5.26 \times 10^3$ ).  $^{31}\text{P}$  NMR (DMF,  $\delta$  ppm):  $-28.7$ .

### 3.3. X-ray crystallography

Data were collected with a Bruker SMART CCD area detector using graphite monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at room temperature. All empirical absorption corrections were applied by using the SADABS program [31]. The structures were solved using direct methods and the corresponding non-hydrogen atoms were refined anisotropically. All the hydrogen atoms of the ligands were placed in calculated positions with fixed isotropic thermal parameters and included in the structure factor calculations in the final stage of full-matrix least-squares refinement. All calculations were performed using the SHELXTL system of computer program [32]. Details of the crystal parameters, data collection and refinement for compound **1** are listed in Table 1, and selected bond distances and angles are given in Table 2.

## 4. Conclusions

In the presence of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and dppm, the reaction of two TCNQ molecules by [2+2] cycloaddition forms a *p*-tricyanovinylphenyldicyanomethide ion ( $\text{PCQ}^-$ ). The reactivity of TCNQ with other metal complexes is being under further investigation.

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## Appendix A. Supplementary material

CCDC 728883 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorgchem.2009.06.016](https://doi.org/10.1016/j.jorgchem.2009.06.016).

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