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# Magnetic Properties of CT Complexes between 2,2″,5,5″-Tetrakis(dimethylamino)terphenyls and TCNQF$_4$

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2,2″,5,5″-Tetrakis(dimethylamino)-*p*- and *m*-terphenyls (**1** and **2**), in which two $N,N,N',N'$-tetramethyl-*p*-phenylenediamine (TMPD) moieties are linked through *p*- and *m*-phenylene units, respectively, were synthesized, and their CT complexes with TCNQF$_4$ were prepared. In the complexes, **1** and **2** possess two $S=1/2$ spins per molecule. The intramolecular interaction between the spins of the two TMPD moieties was found to be antiferromagnetic ($2J/k=-42$ K) in **1**, and ferromagnetic ($2J/k=240$ K) in **2**.

$N,N,N',N'$-Tetramethyl-*p*-phenylenediamine (TMPD) is one of the most readily oxidizable donors, and the magnetic properties of some salts of its cation radical or charge-transfer complexes have been studied in detail.[1)] For example, TMPD perchlorate and tetrafluoroborate salts[1a)] undergo phase transitions at about 190 K due to dimerization, whereas no phase transition was observed in iodide salt.[1b)] In the case of CT complexes, both very weakly and strongly paramagnetic species are known in the literature; TMPD–TCNQ is weakly paramagnetic,[1c)] while TMPD–TCNQF$_4$ shows extremely strong paramagnetism.[1d)]

In this study, 2,2″,5,5″-tetrakis(dimethylamino)-*p*- and *m*-terphenyls (**1** and **2**) that have two TMPD moieties linked through *p*- and *m*-phenylene units, respectively, were synthesized, and the magnetic properties of their CT complexes with TCNQF$_4$ were examined. When **1** and **2** are oxidized into the corresponding dications with suitable acceptors, each TMPD moiety will become a monocation radical and possess an unpaired electron, i.e., a spin of $S=1/2$. There are two cases in which both the spins interact with each other intramolecularly. Ferro- and antiferromagnetic interaction between the two spins would lift the degeneracy and result in a ground-state triplet ($S=1$) and a singlet ($S=0$) species, respectively. When intramolecular ferromagnetic interaction is strong, it might also be possible to effect intermolecular spin alignment in the CT complexes. When there is no intramolecular interaction, the two $S=1/2$ spins would be isolated, and the singlet and triplet states would remain degenerate.

The mode of intramolecular magnetic interaction between two neutral radicals through a $\pi$-conjugated bridging unit has been fully studied.[2)] *m*- and *p*-Phenylene units have been generally accepted to serve as robust ferro- and antiferromagnetic coupling units, respectively. However, there are few analogous precedents concerning the interaction of two cation radicals. Recently, Yoshizawa et al. reported that the cationic triradical of 1,3,5-tris(diphenylamino)benzene had a quartet ground state in a CH$_2$Cl$_2$ glass.[3)] In a poly(*m*-phenyleneoctatetraene-1,8-ylene) derivative doped with AsF$_5$, the behavior of a species with $S\geqq 2$ was observed, though its spin source is a polaron.[4)] On the other hand, the monoanion of *m*-phenylenebis(phenylmethylene) is not ground-state quartet, but doublet.[5)] In view of these limited examples, it is of great interest and importance to investigate the interaction between the two spins of the dications of **1** and **2**. Since $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$ possess resonance structures $\mathbf{1b}^{2+}$ and $\mathbf{2b}^{2+}$, respectively, $\mathbf{1}^{2+}$ is expected to be ground-state singlet, whereas $\mathbf{2}^{2+}$ triplet (Chart 1). Furthermore, the CT complexes containing **2** may exhibit interesting magnetic properties.

## Results and Discussion

Compounds **1** and **2** were synthesized by employing the Pd(0)-catalyzed cross-coupling reactions (Scheme 1).[6)]

The treatment of *p*-diiodobenzene with two equivalents of 2,5-bis(dimethylamino)phenylzinc chloride (**3**) in the presence of the Pd(0) catalyst yielded **1** readily. The use of *m*-diiodobenzene under similar conditions resulted in the formation of one C–C bond by a reaction of the only one iodine atom, i.e., **4** instead of **2**. This is probably due to greater steric hindrance in **4** than in the corresponding *p*-isomer. The isolated **4** was again allowed to react with an excess of **3**, giving a mixture containing **2**. However, it was oxidized to some extent even on deactivated alumina, and its purification proved to be difficult. A small amount of the

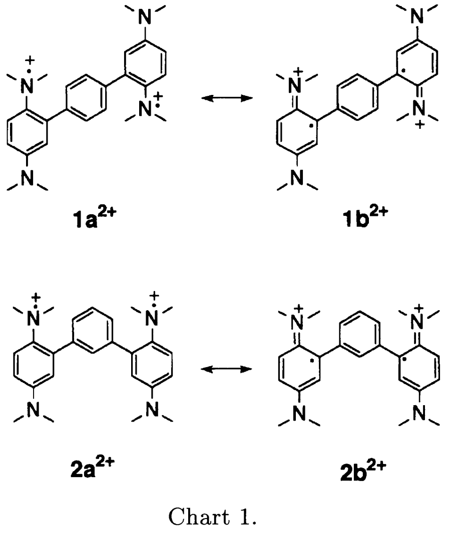
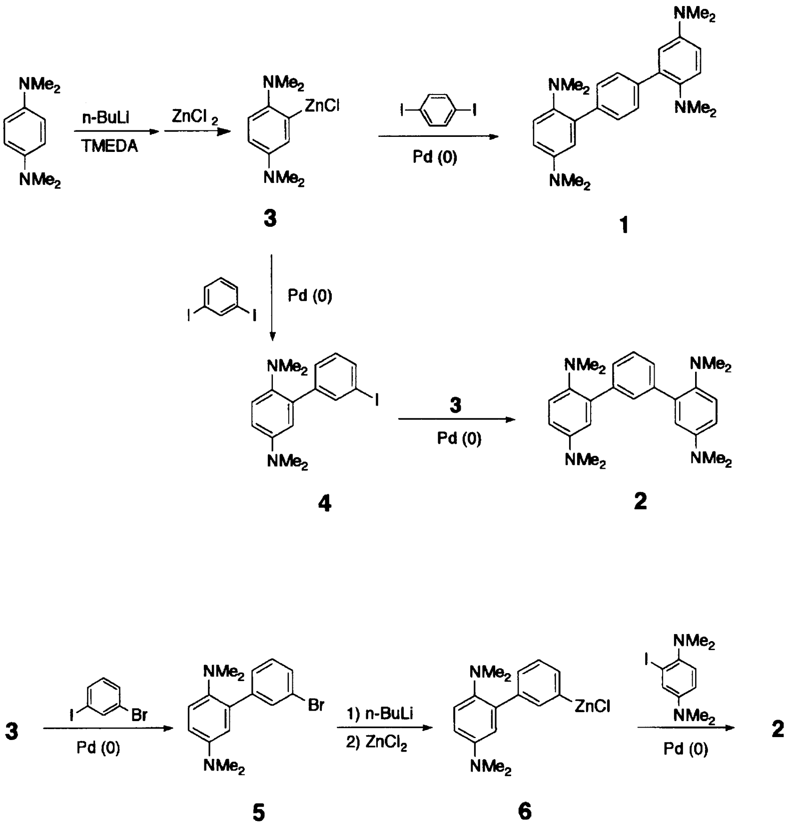


Chart 1.



Scheme 1.

starting material, TMPD, could not be removed completely from **2**. Therefore, another route was employed for the synthesis of **2**. The bromide **5** was prepared in a manner similar to **4** and converted to zinc derivative **6**. Coupling of **6** with 2-iodo-TMPD and subsequent column chromatography made it possible to obtain pure **2**.

The oxidation potentials of **1** and **2** were measured in $CH_3CN$ by cyclic voltammetry (CV) at room temperature. Each voltammogram showed two reversible two-electron oxidation waves, indicating that the two TMPD moieties in each compound are oxidized almost at the same time, first leading to two monocation radicals and next to two dications; the electronic interaction between the two TMPD moieties may not be very strong. The oxidation potentials were $-0.05$ and $+0.38$ V for **1**, and $-0.04$ and $+0.39$ V for **2**, which were nearly equal to those of other aryl-substituted TMPD derivatives such as **4** and **5**.

Some acceptors were tested in order to obtain CT complexes with **1** or **2**. When a $CH_2Cl_2$ solution of DDQ was added to that of **1**, only a blue oily product was formed. It became yellowish soon and could not be isolated. On the other hand, treatment of a hot solution of TCNQF$_4$ in $CH_3CN$ with that of **1** gave a blue solid product. Its appearance remained unchanged at least for several months. In the case of **2** and TCNQF$_4$, a blue solid was isolated in the same way. However, all attempts to prepare single crystals were unsuccessful in both cases; the gradual decomposition of the cation and/or anion radicals was suggested by the change in the color of the mixed solution on standing for a long time.

The composition of both the complexes was found to be donor (**1** or **2**) : TCNQF$_4$ = 1 : 2 on the basis of elemental analysis, though the agreement between the experimental and theoretical values was not very good in the case of **2**. Further purification of the complexes was quite difficult; the recrystallization of the once isolated complexes was impossible. An IR absorption due to the C≡N stretching vibration was observed at 2195 $cm^{-1}$, which agreed with that of the monoanion of TCNQF$_4$.[7] Therefore, it is certain that **1** and **2** exist as dication diradicals in the complexes and possess two $S=1/2$ spins per molecule.

ESR spectra were measured for both complexes at 10 K and room temperature. Each spectrum showed only a sharp singlet at about $g=2$; no absorption due to the $\Delta m_S=2$ transition could be found in the observed temperature range.

The magnetic susceptibilities ($\chi$) of the complexes were measured in the temperature range 5—300 K with a SQUID magnetometer. Figures 1(a) and 1(b) show the temperature dependence of $\chi$ and $\chi T$, respectively.

The $\chi$ values for **2**·(TCNQF$_4$)$_2$, the *m*-isomer, increased monotonously as the temperature decreased, while those for **1**·(TCNQF$_4$)$_2$, the *p*-isomer, showed a maximum at 26 K (Fig. 1(a)). The $\chi T$ values decreased

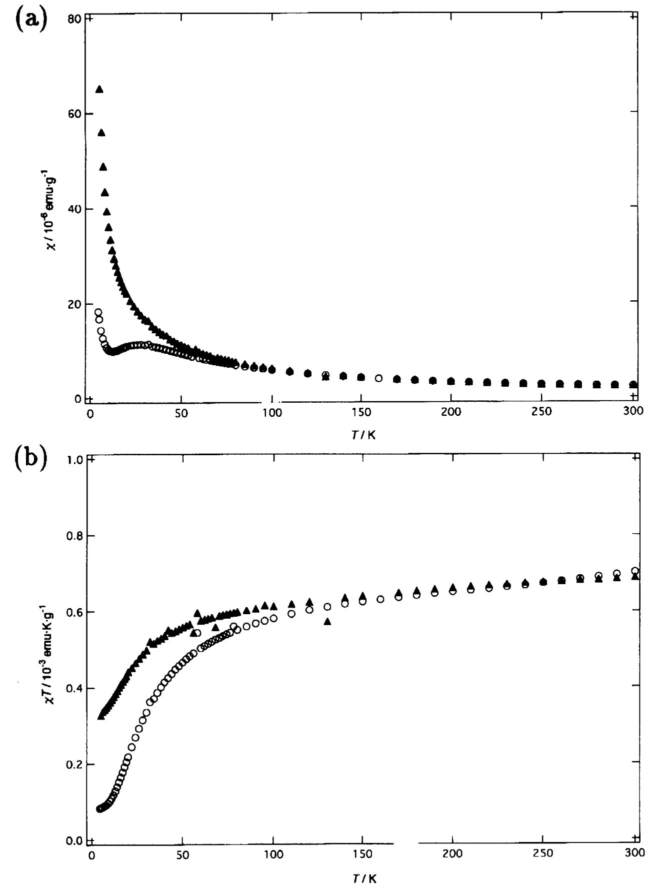


Fig. 1. Temperature dependence of (a) $\chi$ and (b) $\chi T$ for **1**·$(TCNQF_4)_2$ and **2** ·$(TCNQF_4)_2$ obtained at a field of 0.5 T with a SQUID: ○: **1**·$(TCNQF_4)_2$; ▲: **2**·$(TCNQF_4)_2$.

with decreasing temperature in both cases (Fig. 1(b)). The decrease takes place sooner in **1**·$(TCNQF_4)_2$ than in **2**·$(TCNQF_4)_2$. Thus, a distinct difference in the magnetic behavior was observed between the two complexes.

For the interpretation of these data, it is necessary to take into account the magnetic property of the CT complex between TMPD and $TCNQF_4$ (1 : 1) which is regarded as a component of **1** (or **2**)·$TCNQF_4$. Soos et al. reported on the magnetism of the complex TMPD·$TCNQF_4$ in detail, though its crystal structure could not be determined.[1d] According to their measurement, the $\chi$ values for the complex do not follow Curie's law. Instead of employing the Weiss molecular field, they introduced a power-law for intermolecular antiferromagnetic interaction; $\chi$ was proportional to $T^{-a}$ with $a$=0.75±0.10 determined from the plot of log $\chi$ vs. log $T$. In other words, $\chi T$ varies in proportion to $T^{1-a}$, while it would be independent of temperature according to Curie's law.

The analysis of the present data was attempted on the basis of the result by Soos et al., though it is uncertain whether the application of their method is the most appropriate for this case. First, in the case of **2**·$(TCNQF_4)_2$, the temperature dependence of $\chi$ and $\chi T$ is similar to that in TMPD–$TCNQF_4$. In practice, the plot of log $\chi$ vs. log $T$ was found to be almost linear, suggesting that the power-law is valid to some extent also in this case. Thus, the relationship between the $\chi$ and $T$ values in **2**·$(TCNQF_4)_2$ can be roughly expressed by

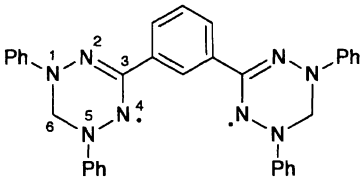
$$\chi = B{\cdot}T^{-A}. \tag{1}$$

The susceptibility of **2**·$(TCNQF_4)_2$ can be explained mainly in terms of the intermolecular interaction between the cation radicals of TMPD moieties and the anion radicals of $TCNQF_4$, which is present in TMPD·$TCNQF_4$. Furthermore, since there should be intramolecular interaction between the two spins in $\mathbf{2}^{2+}$, in order to estimate the magnitude of it more precise fitting was attempted. In addition to Eq. 1, a term based on the population of a triplet relative to a singlet state was taken into consideration, to give

$$\chi = B{\cdot}T^{-A}{\cdot}\frac{4}{3+\exp{(-2J/kT)}}, \tag{2}$$

where $2J$ is a singlet-triplet energy gap. Equation 2 with three parameters ($B$, $A$, and $2J/k$) was fitted to the observed $\chi$ values. Depending on the initial parameter values chosen, the following two sets of best fitting parameters were obtained: $B=(2.0\pm0.1)\times10^{-4}$, $A=0.75\pm0.01$, $2J/k=(1.6\pm0.8)$ K or $B=(1.6\pm0.02)\times10^{-4}$, $A=0.76\pm0.005$, $2J/k=(240\pm72)$ K. Fitting was dominated by the $T^{-A}$ term and less sensitive to positive $J$ value. The former $2J/k$ value corresponds to the absence of intramolecular interaction, while the latter indicates strong ferromagnetic interaction. Since the deviation from the observed values is smaller in the latter case than in the former and ferromagnetic interaction should generally arise between the two spins located at *m*-position of a benzene ring, the latter value seems more likely. In order to support this interpretation, it is necessary to examine the degree of the spin polarization on the benzene rings. Though it is difficult to obtain reliable spin distribution in $\mathbf{2}^{2+}$ by theoretical calculations because of its large size, that of cation radical of TMPD itself is known in the literature.[8,9] The spin density ($\rho$) is considerably localized at the nitrogen atoms and those at $C_2$, $C_3$, $C_5$, and $C_6$ of $TMPD^+$ are about 0.07 on the basis of the HMO calculation or the hyperfine coupling constants due to hydrogen. The spin density distribution in the TMPD moieties of $\mathbf{2}^{2+}$ should not be far from this value; the $\rho$ value at the carbon atoms directly attached to the central benzene ring in $\mathbf{2}^{2+}$ will be smaller than 0.1. This value is comparable to, for example, that of $C_3$ of biradical **7** ($\rho$=0.04),[10] whose ground state is triplet with $2J/k$>300 K (Chart 2).[11] Therefore, it is reasonable that the intramolecular interaction ($2J/k$) in $\mathbf{2}^{2+}$ is also strongly ferromagnetic (240 K) rather than quite weak (ca. 0).

On the other hand, it is evident from Fig. 1(a) that



**7**

Chart 2.

the observed $\chi$ values of **1**·$(TCNQF_4)_2$ do not follow even the power-law. This behavior is expected to be due to antiferromagnetic intramolecular interaction, in contrast with the case of **2**. On the basis of this assumption, the $\chi$ value for **1**·$(TCNQF_4)_2$ can also be expressed by Eq. 2 ($A$=0.76). Furthermore, since the presence of an impurity monoradical was suggested by the increase in the $\chi$ values at low temperature, a term due to this species was added:

$$\chi = B \cdot T^{-0.76} \cdot \frac{4}{3+\exp(-2J/kT)} + \frac{C}{T}. \qquad (3)$$

By fitting Eq. 3 to the observed values (Fig. 2), $B$, $2J/k$, and $C$ were determined as $1.9\times10^{-4}$, $-42$ K ($2J=-31$ cm$^{-1}$), and $8.4\times10^{-5}$ emu·K·g$^{-1}$, respectively. This $C$ value corresponds to about 3% of the total spins.

In conclusion, the intramolecular interaction between the spins of the two TMPD moieties was antiferromagnetic in $\mathbf{1}^{2+}$, and ferromagnetic in $\mathbf{2}^{2+}$. This result is in good agreement with the case of two neutral radicals. However, antiferromagnetic intermolecular interaction is so strong that spin alignment has not been observed even in the complex **2**·$(TCNQF_4)_2$.

## Experimental

**General.** Melting points were determined on a Meltemp apparatus and are uncorrected. IR spectra were recorded on a Hitachi I-504 FT-IR spectrophotometer. $^1$H and $^{13}$C NMR spectra were measured on a JEOL GX-270 spectrometer. The chemical shifts are given in $\delta$ values from $Me_4Si$ as the internal standard in $CDCl_3$. Mass spectra were recorded on a JEOL JMS-SX 102A spectrometer. Cyclic voltammetry (CV) was performed on a Hokuto HA-501 potentiostat/galvanostat and a Hokuto HB-111 function generator. The working electrode was a platinum disk, the counter electrode a platinum wire, and the reference electrode an Ag/Ag$^+$. Measurements were run at room temperature on a 3—5 mM solution (1 M=1 mol dm$^{-3}$) of the sample in $CH_3CN$ containing 0.1 M $n$-$Bu_4NClO_4$ as the supporting electrolyte. Voltammograms were recorded on a Watanabe WX-4401 X-Y recorder at a sweep rate of 100 mV s$^{-1}$. ESR spectra were obtained on a Bruker ESP 300 X-band (9.4 GHz) spectrometer equipped with a Hewlett Packard 5350B microwave frequency counter. For cryogenic measurements, an Air Products Helitran LTR-3-110 cryostat was attached to it. Magnetic susceptibility data were obtained using a Quantum Design model MPMS SQUID magnetometer/susceptometer. Curve fittings of Eqs. 2 and 3 to the observed data were made using a software program Igor on a Macintosh computer.

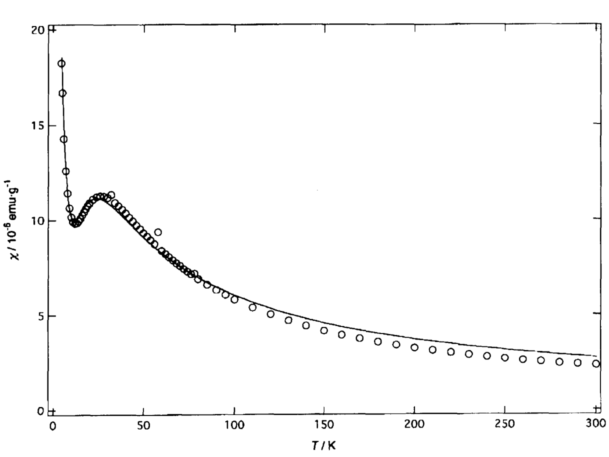


Fig. 2. Best fitting of a theoretical $\chi$–$T$ curve to the observed values for **1**·$(TCNQF_4)_2$.

**2, 2'', 5, 5''- Tetrakis(dimethylamino)- *p*- terphenyl (1).** To a solution of $N,N,N',N'$-tetramethyl-$p$-phenylenediamine (1.64 g, 10.0 mmol) in hexane (20 ml) were added $N,N,N',N'$-tetramethylethylenediamine (1.6 ml, 10.6 mmol) and 1.6 M butyllithium hexane solution (6.4 ml, 10.2 mmol) at room temperature under argon atmosphere. The mixture was stirred at room temperature for 4 h, during which white precipitates appeared. After the mixture was cooled to 0 °C, a solution of anhydrous $ZnCl_2$ (1.40 g, 10.3 mmol) in THF (22 ml) was added to it. The resulting mixture was stirred at 0 °C for 1 h, giving 2,5-bis(dimethylamino)phenylzinc chloride (**3**) as a solution.

A Pd(0) catalyst was prepared in a separate flask by treating $[PdCl_2(PPh_3)_2]$ (351 mg, 0.5 mmol) suspended in THF (13 ml) with 1 M solution of $i$-$Bu_2AlH$ in hexane (1.0 ml, 1.0 mmol) at 0 °C. To this catalyst were added first a solution of $p$-diiodobenzene (1.65 g, 5.0 mmol) in THF and then the solution of **3** prepared above. After being stirred at room temperature overnight, the reaction mixture was quenched with water and extracted with ether. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on alumina with hexane–$CH_2Cl_2$ to give 730 mg (36%) of **1** as pale yellow crystals: Mp 142—145 °C (hexane–EtOH); $^1$H NMR $\delta$=2.51 (12H, s), 2.92 (12H, s), 6.74 (2H, dd, $J$=3 and 9 Hz), 6.79 (2H, d, $J$=3 Hz), 7.03 (2H, d, $J$=9 Hz), 7.61 (4H, s) (All the signals except for the one at 7.61 ppm were observed with slight broadening due to the formation of the cation radical of **1**.). Found: $m/z$ 402.2787. Calcd for $C_{26}H_{34}N_4$: M, 402.2784.

**3'-Iodo-*N,N,N',N'*-tetramethyl-2,5-biphenyldiylamine (4).** The treatment of $m$-diiodobenzene with two equivalents of **3** in the presence of the Pd(0) catalyst under the same conditions as in **1** did not yield 2,2'',5,5''-tetrakis(dimethylamino)-$m$-terphenyl (**2**), but the title compound **4**. Compound **4** was obtained as a pale yellow oil in 62% yield: $^1$H NMR $\delta$=2.46 (6H, s), 2.89 (6H, s), 6.63 (1H, d, $J$=3 Hz), 6.73 (1H, dd, $J$=3 and 9 Hz), 7.01 (1H, d, $J$=9 Hz), 7.11 (1H, t), 7.58—7.61 (2H, m), 7.92 (1H, t); $^{13}$C NMR $\delta$=41.4, 44.1, 93.9, 113.3, 116.2, 119.5, 128.6, 129.8, 134.5, 135.4, 137.8, 142.1, 144.3, 146.8; MS $m/z$ 366 (M$^+$, base), 296, 220.

**3'- Bromo- *N,N,N',N'*- tetramethyl- 2, 5- biphenyl-**

**diylamine (5).** The treatment of *m*-bromoiodobenzene with one equivalent of **3** under the same conditions as in **4** gave **5** as a yellow oil in 66% yield; $^1$H NMR $\delta$=2.49 (6H, s), 2.90 (6H, s), 6.64 (1H, d, $J$=2.9 Hz), 6.73 (1H, dd, $J$=2.9 and 8.8 Hz), 7.03 (1H, d, $J$=8.8 Hz), 7.24 (1H, t), 7.42 (1H, d), 7.54 (1H, d), 7.74 (1H, t); $^{13}$C NMR $\delta$=41.3, 44.2, 113.3, 116.3, 119.4, 122.0, 127.7, 131.8, 131.9, 134.6, 142.2, 144.2, 146.7.

**2,2″,5,5″-Tetrakis(dimethylamino)-*m*-terphenyl (2).** To a solution of **5** (1.07 g, 3.35 mmol) in THF (15 ml) was added 1.6 M butyllithium hexane solution (2.2 ml, 3.5 mmol) at −78 °C under argon atmosphere. After the mixture was stirred for 15 min, a solution of anhydrous $ZnCl_2$ (490 mg, 3.6 mmol) in THF (10 ml) was added to it. Stirring of the mixture at 0 °C for 1 h gave zinc derivative **6** as a solution. The solution of **6** was treated with 2-iodo-*N*,*N*,*N*′,*N*′-tetramethyl-1,4-phenylenediamine (1.33 g, 4.59 mmol) in the presence of the Pd(0) catalyst (0.15 mmol) under the similar conditions to those of **4**. The usual work-up and column chromatography on alumina (hexane–$CH_2Cl_2$) afforded 380 mg (30%) of **2** as a yellow oil: $^1$H NMR $\delta$=2.50 (12H, s), 2.92 (12H, s), 6.75 (4H, m), 7.02 (2H, d), 7.41 (1H, t, $J$=7.8 Hz), 7.52 (2H, d, $J$=7.8 Hz), 7.88 (1H, t). The former four signals, which were assigned to the protons on the two TMPD moieties, were observed with considerable broadening due to the formation of the cation radical of **2**. Found: $m/z$ 402.2772. Calcd for $C_{26}H_{34}N_4$: M, 402.2784.

**$1\cdot(TCNQF_4)_2$.** To a hot solution of **1** (5 mg, 0.012 mmol) in $CH_3CN$ was added $TCNQF_4$ (7 mg, 0.025 mmol) dissolved in $CH_3CN$, and the mixture was kept at 0 °C, giving a blue powder (7 mg, 59%): Mp 158—160 °C (decomp); IR (KBr) $\nu_{CN}$=2195 cm$^{-1}$. Found: C, 62.60; H, 3.75; N, 17.76%. Calcd for **1**:$TCNQF_4$=1:2 ($C_{50}H_{34}N_{12}F_8$): C, 62.89; H, 3.59; N, 17.60%.

**$2\cdot(TCNQF_4)_2$.** A blue powder was obtained from **2** (15 mg) and $TCNQF_4$ (24 mg) by the above method in 50% yield: Mp 145—148 °C (decomp); IR (KBr) $\nu_{CN}$=2195 cm$^{-1}$. Found: C, 61.61; H, 3.67; N, 16.86%.

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