# The Synthesis of 2,7-Bis(dimethylamino)pyrene and -tetrahydropyrene and the Electrical Conductivities of Their Complexes[1)]

Naomi UEDA, Bunji NATSUME, Kazumi YANAGIUCHI, Yoshiteru SAKATA,*
Toshiaki ENOKI,† Gunzi SAITO,† Hiroo INOKUCHI,† and Soichi MISUMI*
*The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567*
† *The Institute for Molecular Science, Okazaki, Aichi 444*

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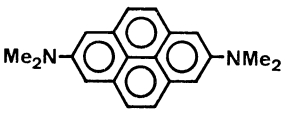
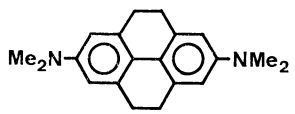
New π-donors containing a pyrene or a tetrahydropyrene ring were synthesized by means of a unique transannular reaction of the corresponding [2.2]metacylcophane derivatives. The CT complexes of these donors with a series of TCNQ derivatives different in electron affinity were prepared, and their electrical conductivities on single crystals were measured. The highest conductivity (0.36 $\Omega^{-1}$ cm$^{-1}$) was that of the tetrahydropyrene derivative–TCNQ complex. It was reconfirmed that the partial charge-transfer from a donor to an acceptor is very important for high conductivity.

A wide variety of charge-transfer (CT) complexes with a metal-like conductivity have recently been prepared. Many such highly conductive CT complexes or salts are composed of chalcogen atom-containing π-donors like TTF. Several heterocyclic donors containing one or two nitrogen atoms in condensed-ring systems also give highly conductive CT complexes, *e.g.*, *N*-methylphenazinium–TCNQ[2)] and quinolinium–TCNQ[3)] complexes.

On the other hand, a fairly high conductivity (2 $\Omega^{-1}$ cm$^{-1}$ with a compressed sample) has been reported for the TCNQ complex of a diamino derivative of a carbocyclic hydrocarbon, 1,6-diaminopyrene.[4)] The conductivity of a single crystal can usually be expected to be increased by $10^2$ times the conductivity on the corresponding pressed pellet. This excellent conductivity prompted us to prepare the complex of 2,7-bis(dimethylamino)pyrene **1**, which has a higher symmetry ($D_{2h}$) than 1,6-diaminopyrene ($C_{2h}$). Bis(dimethylamino)tetrahydropyrene **2**, a precursor in the present synthetic course for **1**, is also interesting in connection with the study[5)] of the relationship between the conductivity and the crystal structure of a series of benzidine–TCNQ complexes.




**1**

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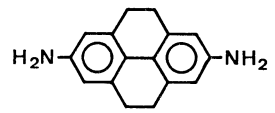
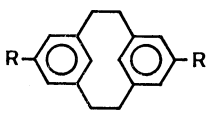



**3**




**4** R = $CH_2Br$
**5** R = CHO
**6** R = $CO_2H$
**7** R = $NH_2$
**8** R = $NMe_2$

## Results and Discussion

*Synthesis.* Because of the high electron density at the 1-position in the highest occupied molecular orbital (HOMO), pyrene is much more subjected to electrophilic substitution at this position than the others. Therefore, it is difficult to prepare 2,7-disubstituted pyrene by the electrophilic substitution reaction of pyrene itself. Furthermore, the solubility of pyrene derivatives is generally low in usual organic solvents. These facts forced us to choose a synthetic route which leads to the substituted pyrene chromophore in the final step.

According to the literature,[6)] 5,13-bis(bromomethyl)-[2.2]metacyclophane **4** was prepared *via* four steps starting from mesitylene. The Sommelet reaction of **4** was carried out in the usual manner to give **5** in a 72% yield. The oxidation of **5** with potassium permanganate gave **6** quantitatively. The Curtius reaction of **6** *via* acid chloride, acid azide, and isocyanate yielded a diamino compound **7** in a 64% yield. The diamine **7** was converted to **8** with dimethyl sulfate in an 86% yield.

The ready transformation of substituted [2.2]metacyclophane to the tetrahydropyrene framework has been reported by Allinger *et al.*[7)] and by Sato *et al.*[8)] Since then, this unique reaction has been utilized by several groups in the synthesis of substituted tetrahydropyrenes and pyrenes.[9)] We also have been employed this elegant reaction as a key step in the synthesis of **1**—**3**. Thus, the transannular dehydrogenative ring contraction of **7** and **8** with DDQ gave **3** (93% yield) and **2** (96% yield) respectively. The tetrahydro compound **2** was further dehydrogenated with Pd–C in boiling decalin to yield **1** in a 49% yield. The complexation of **1**—**3** was carried out with π-acceptors, such as TCNQ derivatives and chloranil. Single crystals of these CT complexes were obtained by the diffusional method or by recrystallization. The details will be described in the experimental part. The donor-to-acceptor ratio was determined by elemental analysis to be 1:1 for all the complexes.

*Cyclic Voltammetry.* Cyclic voltammetry was carried out in acetonitrile containing 0.1 M** of tetraethylammonium perchlorate as a supporting electrolyte and with an SCE reference electrode. The voltammograms of **1**—**3** are shown in Fig. 1. In each curve in the figure, two oxidation waves are observed. Both waves of **2** and **3** and the first wave of **1** are reversible,

** 1 M = 1 mol dm$^{-3}$.

whereas the second one of **1** is irreversible. The half-wave potentials ($E_{1/2}$) of these compounds are summarized in Table 1, together with those of the reference compounds, **9**—**11**. Of the three new donors, **2** shows the lowest value, one which is close to that of the powerful donor **11**. It should be pointed out that the value of **2** is lower by 0.20 V than that of **10**. This observation is particularly surprising in view of the fact that **2** and **10** have the same chromophore, 4,4'-diaminobiphenyl. A similar extent of difference (0.12 V) was also observed between the potentials of **3** and **9**. These data clearly indicate that the planar structure of a biphenyl chromophore forced by two ethylene chains plays an important role in lowering the oxidation potential. Furthermore, the value of **2** remains lower than that of **1**, which has a more condensed aromatic ring than the biphenyl. This might be interpreted as follows. The electron density at the 2- and 7-positions of pyrene at the HOMO level is zero. Hence, the ionization potential of the pyrene is subject to only a small influence of the substituents attached to these positions. The SCF-CI calculation by Nogami[10] showed that the ionization potentials of 1,6-, 1,8-, and 2,7-diaminopyrenes are 6.63, 6.64, and 7.39 eV respectively, supporting the interpretation stated above.

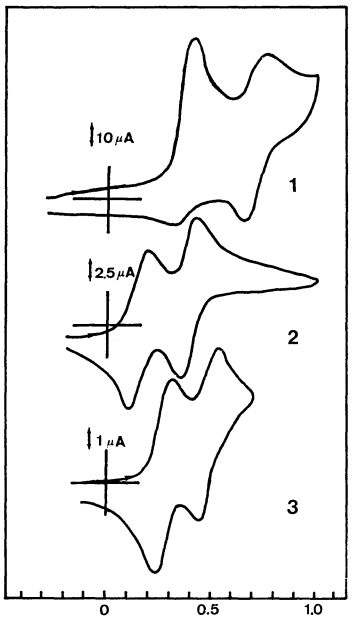
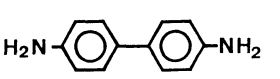


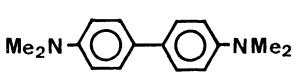

Fig. 1. Cyclic voltammograms of compounds, **1**, **2**, and **3**, in $CH_3CN$ using $Et_4NClO_4$ as a supporting electrolyte.

Table 1. Half-wave potentials $E_{1/2}$ of **1**—**3** **9**—**11**

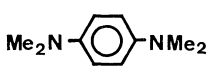
| | ($E^1_{1/2}$ *vs.* SCE)/V | ($E^2_{1/2}$ *vs.* SCE)/V |
|---|---|---|
| **1** | 0.37 | 0.71 |
| **2** | 0.14 | 0.38 |
| **3** | 0.31 | 0.49 |
| **9** | 0.43 | 0.69 |
| **10** | 0.34 | 0.52 |
| **11** | 0.04 | 0.63 |



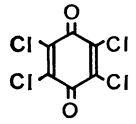

**9**



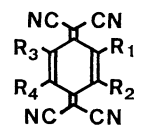

**10**




**11**




**13**




**12** a $R_1 = R_2 = R_3 = R_4 = H$

b $R_1 = R_2 = R_3 = R_4 = F$

c $R_1 = F, R_2 = R_3 = R_4 = H$

d $R_1 = R_3 = Me, R_2 = R_4 = H$

e $R_1 = R_3 = OMe, R_2 = R_4 = H$

In order to evaluate a relative acceptor strength, we determined the half-wave reduction potentials of six $\pi$-acceptors, TCNQ **12a**, $TCNQ(F)_4$ **12b**,[11] TCNQ(F) **12c**,[12] $TCNQ(Me)_2$ **12d**,[11] $TCNQ(OMe)_2$ **12e**,[11] and chloranil **13**, as is shown in Table 2.

*Infrared Spectra.* The frequencies of C≡N stretching vibrations of CT complexes are shown in Table 3, together with those of composite acceptors and their potassium salts. With these values, the degree of charge-transfer ($\rho$) in the complexes was calculated according to this equation:[13]

$$\rho = (\nu^{acc}_{C\equiv N} - \nu^{com}_{C\equiv N})/(\nu^{acc}_{C\equiv N} - \nu^{salt}_{C\equiv N})$$

Table 2. Half-wave potentials $E_{1/2}$ of **12** and **13**

| | ($E^1_{1/2}$ *vs.* SCE)/V | ($E^2_{1/2}$ *vs.* SCE)/V |
|---|---|---|
| **12b** | 0.50 | −0.04 |
| **12c** | 0.22 | −0.33 |
| **12a** | 0.12 | −0.43 |
| **12d** | 0.05 | −0.42 |
| **12e** | −0.08 | −0.55 |
| **13** | −0·06 | −0.82 |

Table 3. Wavenumbers of $\nu_{C\equiv N}$ in acceptors **12**, their $K^+$ salts, and CT complexes with **1**—**3** and degree of charge transfer ($\rho$) in the complexes[a]

| Donor | Acceptor | $\nu^{acc}_{C\equiv N}$/cm$^{-1}$ | $\nu^{com}_{C\equiv N}$/cm$^{-1}$ | $\nu^{salt}_{C\equiv N}$/cm$^{-1}$ | $\rho$ |
|---|---|---|---|---|---|
| **1** | **12a** | 2220 | 2210 | 2185 | 0.29 |
| **1** | **12d** | 2225 | 2205 | 2185 | 0.50 |
| **2** | **12a** | 2220 | 2200 | 2185 | 0.57 |
| **2** | **12b** | 2220 | 2195 | 2195 | 1.00 |
| **2** | **12c** | 2215 | 2190 | 2180 | 0.71 |
| **2** | **12d** | 2225 | 2210 | 2185 | 0.38 |
| **2** | **12e** | 2205 | 2200 | 2180[b] | 0.20 |
| **3** | **12a** | 2220 | 2195 | 2185 | 0.71 |
| **3** | **12d** | 2225 | 2210 | 2185 | 0.63 |

a) $\nu^{acc}_{C\equiv N}$, $\nu^{com}_{C\equiv N}$, and $\nu^{salt}_{C\equiv N}$ are C≡N stretching vibrations of **12**, CT complexes, and $K^+$ salts respectively. b) Value of sodium salt.

Table 4. Electrical conductivities ($\sigma$) at room temperature and activation energies ($E_a$) of CT complexes of **1**—**3** and related donors on single crystals

| | $\sigma/\Omega^{-1}\,cm^{-1}$ | $E_a$/eV |
|---|---|---|
| **1**—**12a** | $1.95\times10^{-5}$ | 0.32 |
| **1**—**12d**[a] | $2.86\times10^{-11}$ | 0.52 |
| **1**—**13**[a] | $5.13\times10^{-13}$ | 0.95 |
| **2**—**12a** | 0.358 | 0.50 |
| **2**—**12b** | $6.90\times10^{-6}$ | 0.37 |
| **2**—**12c** | $1.05\times10^{-2}$ | 0.53 |
| **2**—**12d** | $8.26\times10^{-5}$ | 0.19 |
| **2**—**12e** | $2.38\times10^{-6}$ | 0.31 |
| **2**—**13** | $1.01\times10^{-10}$ | —[b] |
| **3**—**12a**[a] | $5.30\times10^{-7}$ | 0.53 |
| **3**—**12d**[a] | $5.46\times10^{-9}$ | 0.53 |
| **3**—**13** | $5.52\times10^{-10}$ | 0.53 |
| **10**—**12a** | $6.49\times10^{-6}$ | 0.32 |
| **9**—**12a**[a] | $6.99\times10^{-12}$ | 0.54[5] |

a) Compressed pellet. b) The activation energy could not be determined because the very weak current was hard to detect.

The values are summarized in the same table, showing the distribution of $\rho$ values between unity and 0.20. A linearity is obtained when the $\rho$ values of the complexes **1**—**12** are plotted against the half-wave potentials, $E^1_{1/2}$, of the acceptors in Table 2. This reveals a close relationship between these two values.

*Electrical Conductivity.* All the complexes show typical semiconducting behavior in the temperature range measured. Table 4 summarizes the electrical conductivities ($\sigma$) of these complexes on a single crystal at room temperature and the activation energies ($E_a$) based on the temperature dependence of the resistivities. The data on **9**–TCNQ given by Takahashi *et al.*[5] are included for purposes of comparison. In contrast to the high conductivity of 1,6-diaminopyrene–TCNQ on a compressed sample, the value of **1**–TCNQ is lower, even on a single crystal. This may be due to the relatively high $E^1_{1/2}$ value of **1**, as may be seen in Table 1. On the other hand, **2** with low $E^1_{1/2}$ value forms better conducting CT complexes than does **1**. It is noteworthy that, of the fourteen CT complexes in the table, **2**–TCNQ showed the highest conductivity, larger by $10^5$ times than that of **10**–TCNQ, despite bearing the same diaminobiphenyl chromophore in **2** and **10**. A difference of similar extent ($10^5$) was also observed between **3**–TCNQ and **9**–TCNQ. Possibly these results are mainly due to the difference in the oxidation potential between **2** and **10** or between **3** and **9**, as may be seen in Table 1, and partly due to the different packing in a crystal, based on the different extent of planarity between biphenyl and tetrahydropyrene chromophores, although the molecular structures of these complexes are not yet known.

In Fig. 2 the conductivities of a series of complexes of **2** are plotted against the $E^1_{1/2}$ values of the acceptors. A noticeable point is that the conductivity of **2**–TCNQ is the highest. Not only the weaker acceptors, but also stronger acceptors than TCNQ itself diminish the conductivities of the complexes with **2**. In other words, the introduction of substituents to the TCNQ ring results in a decrease in the conductivities of the complexes, apart from the kind of the substituent. This fact clearly indicates that the incomplete electron transfer[14] from a donor to an acceptor has a significant effect on the high conductivity of the charge-transfer complexes.

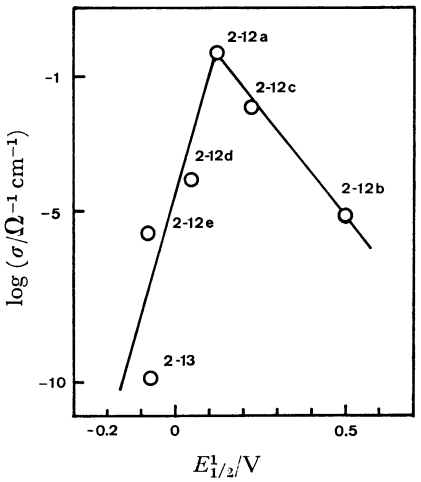



Fig. 2. Plots of conductivities of complexes, **2**—**12** and **2**—**13**, *vs.* $E^1_{1/2}$ of acceptors.

## Experimental

All the melting points are uncorrected. The IR, NMR, MS, and electronic spectra were recorded with a Hitachi EPI-G2 and a Hitachi 345, a JEOL JNM-FX-100 (100 MHz for $^1$H), a Hitachi RMU-7, and a Hitachi EPS-3T spectrometer respectively.

The cyclic voltammetry was carried out at room temperature under argon using the combination of a generator, Hokuto HB-107A, and a potentiostat, Hokuto HA-104. A glassy carbon electrode (Yanagimoto P-13) was used as the anode, and platinum wire was used as the counter electrode.

The electrical resistances for the pressed pellet and for the single crystal were measured with the two probe methods in the region from room temperature down to the temperature where an electrometer (Keithley 616) reached the lower limit of the detectable current ($10^{-14}$ A). The electrical constants were obtained using silver paint (Du Pont 4817). The sizes of the single crystals were measured with a profile projector, Nikon V-24B.

[*2.2*]*Metacyclophane-5,13-dicarbaldehyde (5).* To a solution of 5,13-bis(bromomethyl)[2.2]metacyclophane **4**[6] (6.17 g, 15.6 mmol) in chloroform (60 ml) was added hexamethylenetetramine (5.10 g, 35.9 mmol), then the mixture was refluxed for 4 h. After cooling, a precipitate (ammonium salt) was collected and dried. A solution of this salt in 50% acetic acid (80 ml) was refluxed for 15 h. The crystals thus yielded were collected, washed with water, and dried. The subsequent recrystallization of the product from acetone gave **5** (2.98 g, 72% yield).

**5**: Colorless needles; mp 235—236.5 °C. $^1$H NMR ($CDCl_3$) $\delta$=3.23, 3.30 (d, $J$=8 Hz, 8H, $CH_2$), 4.52 (t, $J$=2 Hz, 2H, inner ArH), 7.65 (d, $J$=2 Hz, 4H, outer ArH), 10.04 (s, 2H, CHO). IR (Nujol mull) 2800, 2720, 1690 cm$^{-1}$.

Found: C, 81.57; H, 5.89%. Calcd for $C_{18}H_{16}O_2$: C,

Table 5. Properties and analytical data of CT complexes of **1**—**3**

| Complex | Solvent | Yield % | Found (Calcd)[c] (%) C | H | N | Cl | Mp $\theta_m$/°C | Remarks | Size/mm³ [d] |
|---|---|---|---|---|---|---|---|---|---|
| **1**—**12a**[a] | $CH_3CN$ | 95 | 78.03 (78.03) | 4.76 (4.91) | 16.94 (17.06) | | decomp>230 | Fine black needles | 0.048×0.040×2.553 |
| **1**—**12d**[a] | $CH_3CN$ | 89 | 78.73 (78.44) | 5.26 (5.42) | 15.89 (16.14) | | decomp>248 | Fine dark brown needles | 2×2×0.97[e] |
| **1**—**13**[b] | Benzene | 84 | 58.48 (58.45) | 3.64 (3.77) | 5.13 (5.24) | 26.39 (26.54) | decomp>280 | Black micro-crystals | 2.5×2.5×1.01[e] |
| **2**—**12a**[a] | $CH_3CN$ | 92 | 77.66 (77.39) | 5.67 (5.68) | 17.15 (16.92) | | decomp>223 | Long dark violet columns | 0.197×0.198×4.687 |
| **2**—**12b**[a] | $CH_3CN$ | 62 | 67.10 (67.60) | 4.07 (4.25) | 14.78 (14.78) | | 187—189 | Dark bluish green needles | 0.127×0.687×2.826 |
| **2**—**12c**[a] | $CH_3CN$ | 71 | 74.72 (74.69) | 5.19 (5.29) | 16.45 (16.33) | | 201—203 | Dark purple needles | 0.120×0.129×3.859 |
| **2**—**12d**[b] | THF | 82 | 77.63 (77.83) | 6.14 (6.15) | 15.72 (16.02) | | 207—208 | Dark violet needles | 0.048×0.040×1.194 |
| **2**—**12e**[b] | $CH_3CN$ | 55 | 73.22 (73.36) | 5.82 (5.79) | 15.20 (15.10) | | 181—183 | Long dark violet columns | 0.090×0.076×1.847 |
| **2**—**13**[b] | THF | 75 | 57.88 (58.01) | 4.49 (4.49) | 5.04 (5.20) | 26.55 (26.34) | decomp>340 | Long black columns | 0.123×0.019×1.122 |
| **3**—**12a**[b] | $CH_2Cl_2$ | 82 | 76.05 (76.35) | 4.33 (4.58) | 18.82 (19.08) | | decomp>170 | Dark violet needles | 2.522×2.522×1.601[e] |
| **3**—**12d**[b] | $CH_2Cl_2$ | 82 | 76.72 (76.90) | 5.04 (5.16) | 18.03 (17.94) | | 183.5—185 | Black needles | 2.534×2.534×0.459[e] |
| **3**—**13**[b] | $CH_2Cl_2$ | 71 | 55.00 (54.80) | 3.55 (3.34) | 5.97 (5.81) | 29.65 (29.41) | decomp> 142 | Long black columns | 2.519×2.519×0.364[e] |
| **10**—**12a**[a] | $CH_3CN$ | 80 | 75.39 (75.65) | 5.16 (5.44) | 18.75 (18.90) | | 219—222 | Dark violet needles | 0.066×0.062×2.294 |

a) Prepared by diffusional method. b) Prepared by mixing and recrystallization. c) Values are calculated assuming that the donor-to-acceptor ratio is 1:1. d) Crystal sizes used for measurement of electrical conductivity. e) Sizes of pellet (radius×radius×thickness).

81.79; H, 6.10%.

*[2.2]Metacyclophane-5,13-dicarboxylic Acid (6).* An aqueous solution (125 ml) of potassium permanganate (4.0 g, 25.3 mmol) was stirred with a solution of dialdehyde **5** (2.5 g, 9.46 mmol) at 60—70 °C for a period of 2 h. After the addition was over, the mixture was stirred for a further hour. To the solution was added 10% aqueous sodium hydroxide (80 ml), and the insoluble material was filtered off. The filtrate was acidified with dil hydrochloric acid. The precipitate was collected, washed with water, and dried to give 2.6 g (93%) of **6**.

**6**: Mp >350 °C. IR (Nujol mull) 1690 $cm^{-1}$. MS *m/e* 296 ($M^+$).

*5,13-Diamino[2.2]metacyclophane (7).* A mixture of dicarboxylic acid **6** (2.6 g, 8.8 mmol) and thionyl chloride (60 ml) was refluxed for 4 h, and the excess thionyl chloride was distilled off. The acid chloride thus obtained was dissolved in THF (80 ml). To the stirred, ice-cooled solution was added an aqueous solution (19 ml) of sodium azide (1.35 g, 20.8 mmol). After additional stirring at room temperature for 1 h, water was added to the solution. The precipitate was collected by filtration, washed with water, and dried. The acid azide is fairly stable and can be handled safely at room temperature. A solution of the azide in benzene (60 ml) was refluxed for 4 h. After cooling, 18 ml of conc hydrochloric acid was added, and the mixture was refluxed for 1 h under nitrogen. The benzene was then removed, and the insoluble material was filtered off. The filtrate was neutralized with aqueous sodium hydroxide. The crystals thus deposited were collected by filtration and washed with water to give 1.33 g (64%) of **7**.

**7**: Colorless prisms from benzene-hexane; mp 232—233 °C with dec. $^1H$ NMR ($CDCl_3$) $\delta$=2.08, 2.91 (d, $J$=8 Hz, 8H, $CH_2$), 4.06 (t, $J$=1.5 Hz, 2H, inner ArH), 6.40 (d, $J$=1.5 Hz, 4H, outer ArH). IR (Nujol mull) 3400, 3290, 3190 $cm^{-1}$.

Found: C, 80.36; H, 7.49; N, 11.87%. Calcd for $C_{16}H_{18}N_2$: C, 80.63; H, 7.61; N, 11.75%.

*5,13-Bis(dimethylamino)[2.2]metacyclophane (8).* To a mixture of **7** (1.70 g, 7.1 mmol) and sodium hydrogencarbonate (4.47 g, 53.2 mmol) in 70 ml of water–THF (3:4) was added dimethyl sulfate (6.08 g, 48.3 mmol) at 0 °C under nitrogen. Stirring was continued at room temperature for 2 h and then at 65—70 °C for 20 min. After cooling, 2-aminoethanol (7 ml) was added, and the mixture was heated at 120 °C (bath temperature) for 9 h with stirring. The THF was then distilled off, and the residue was extracted with dichloromethane. The extracts were washed with a saturated aqueous solution of sodium chloride and dried over $MgSO_4$. After the removal of the solvent, the crude product was passed through a short column of alumina with chloroform–benzene (1:1). Recrystallization from methanol gave 1.79 g (86%) of pure **8**.

**8**: Mp 208—209 °C. $^1H$ NMR ($CDCl_3$) $\delta$=2.14, 2.97 (d, $J$=7.8 Hz, 8H, $CH_2$), 2.96 (s, 12H, Me), 4.04 (t, $J$=1.2 Hz, 2H, inner ArH), 6.48 (d, $J$=1.2 Hz, 4H, outer ArH). IR (Nujol mull) 1595 $cm^{-1}$.

Found: C, 82.26; H, 8.47; 9.29%. Calcd for $C_{20}H_{26}N_2$: C, 82.15; H, 8.27; N, 9.58%.

*2,7-Diaminotetrahydropyrene (3).* To a stirred solution of **7** (200 mg, 0.84 mmol) in benzene (50 ml) was added a solution of dichlorodicyano-*p*-benzoquinone (DDQ) (190 mg) in benzene (40 ml). After additional stirring for 1 h at room temperature and the removal of the benzene, an

aqueous solution of 10% sodium hydroxide was added and the mixture was extracted with dichloromethane. The extracts were washed with a saturated sodium chloride solution and dried. The subsequent removal of the solvent gave 190 mg (95%) of **3**.

**3**: Colorless microcrystals by sublimation; mp 242—243 °C with decomp. $^1$H NMR ($CDCl_3$) $\delta$=2.75 (s, 8H, $CH_2$), 6.40 (s, 4H, ArH). IR (Nujol mull) 3440, 3390, 3180, 1630, 1610 cm$^{-1}$.

Found: C, 81.32; H, 6.82; N, 11.85%. Calcd for $C_{16}H_{16}N_2$: C, 81.11; H, 6.66; N, 11.90%.

*2,7-Bis(dimethylamino)tetrahydropyrene (2). a)*: The methylation of **3** with dimethyl sulfate was done in a manner similar to that used in the synthesis of **8**. The crude product was passed through a short column of alumina. Further purification by sublimation gave 224 mg (96%) of **2**.

**2**: Colorless prisms; mp 142—143 °C. $^1$H NMR ($CDCl_3$) $\delta$=2.84 (s, 8H, $CH_2$), 2.96 (s, 12H, $CH_3$), 6.49 (s, 4H, ArH). UV (MeOH) 220 ($\varepsilon$ 3.86×10$^4$), 321 (3.53×10$^4$), 333 nm (2.96×10$^4$).

Found: C, 82.32; H, 8.36; N, 9.69%. Calcd for $C_{20}H_{24}N_2$: C, 82.15; H, 8.27; N, 9.58%.

*b)*: The transannular reaction of **8** with DDQ was carried out in a manner similar to that described for **3**. The crude product was purified by column chromatography with silica gel and dichloromethane–benzene (1:1) and then by recrystallization from methanol (93% yield).

*2,7-Bis(dimethylamino)pyrene (1).* A mixture of **2** (630 mg, 2.15 mmol), Pd–C (1.378 g), and decalin (50 ml) was refluxed under nitrogen for 1 h. After the filtration of the Pd–C, 2 mol dm$^{-3}$ hydrochloric acid was added to the filtrate. The aqueous layer separated was made basic with 10% sodium hydroxide, extracted with dichloromethane, and the organic layer was dried. After the removal of the solvent, the residue was chromatographed on silica gel containing 10% of water with benzene. Recrystallization from benzene gave 304 mg (49%) of **1**.

**1**: Yellowish orange columns; mp 222—223 °C with dec. $^1$H NMR ($CDCl_3$) $\delta$=3.19 (s, 12H, $CH_3$), 7.55 (s, 4H, ArH), 7.88 (s, 4H, ArH). UV (MeOH) 289 ($\varepsilon$ 1.31×10$^5$), 314 (1.51×10$^4$), 328 (1.20×10$^4$), 344 (2.49×10$^4$), 443 nm (3.29×10$^3$). IR (Nujol mull) 1605 cm$^{-1}$.

Found: C, 83.26; H, 7.18; N, 9.56%. Calcd for $C_{20}H_{20}N_2$: C, 83.30; H, 6.99; N, 9.71%.

*Preparation of Single Crystals of CT Complexes. a) Difusional Method*: In one side of an H-type glass tube was placed **2** (29 mg, 0.1 mmol), and in the other side, TCNQ (20 mg, 0.1 mmol). The apparatus was then gradually filled with acetonitrile under nitrogen and allowed to stand in the dark for 20 d. The black column crystals produced at the middle part of the apparatus were collected, washed with acetonitrile, and dried (46 mg, 95%).

*b) Recrystallization*: Two solutions of **2** (10 mg, 0.07 mmol) and $TCNQ(Me)_2$ (15 mg, 0.07 mmol) in an equal amount (10 ml) of acetonitrile were mixed at room temperature. The precipitate was collected and recrystallized from THF to give 28 mg (82%) of **2**-$TCNQ(Me)_2$ as dark violet needles.

Single crystals of the other complexes were prepared according to method *a*) or *b*). The data of the elemental analyses, melting points, colors, shapes, and crystal sizes of the complexes are summarized in Table 5.

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