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Syntheses and Properties of 11,11,12,12-Tetracyano-2,6-anthraquinodimethane (TANT) and Its 9,10-Dichloro Derivative as Novel Extensive Electron Acceptors

Kazuo Takimiya, Tetsuya Yanagimoto, Takashi Yamashiro, Fumio Ogura,# and Tetsuo Otsubo*

Department of Applied Chemistry, Faculty of Engineering, Hiroshima University,
Kagamiyama, Higashi-Hiroshima 739-8527

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The title compound (TANT) and its 9,10-dichloro derivative (TANT-Cl) have been prepared as higher homologues in an extended electron-acceptor series of TCNQ and TNAP. On the basis of cyclic voltammetry, the accepting ability of TANT is nearly comparable to those of TCNQ and TNAP, and that of TANT-Cl is further enhanced by the chloro substitutuent groups. In addition, TANT and TANT-Cl show an effective reduction of on-site coulombic repulsion, due to their extensive anthraquinone quinonoid system. They thus behave as superior electron acceptors for forming electrically conductive charge-transfer complexes with various electron donors, mostly of the TTT type.

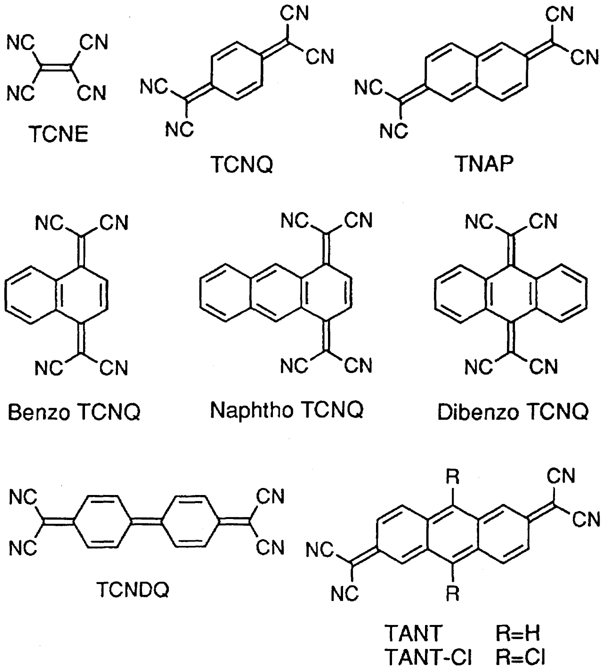

Chart 1.

Since the discovery of the charge-transfer complex of tetrathiafulvalene (TTF) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) as the first organic metal,[1)] the development of new electron donors and acceptors has been of great interest.[2)] Some such efforts have been made while focusing on the designs of extensively conjugated electron donors and acceptors endowed with reduced on-site coulombic repulsion.[3)] Garito and Heeger first noted the importance of a reduced on-site coulombic repulsion by comparing tetracyanoethylene (TCNE) with the quinonoid-inserted electron acceptors, TCNQ and 9,9,10,10-tetracyano-2,6-naphthoquinodimethane (TNAP).[4)] As long as the first reduction potential is used as a measure of electron-accepting strength, the small TCNE acceptor possesses nearly the same ability as do TCNQ and TNAP, but forms no conductive complex (Chart 1). On the other hand, the large TCNQ and TNAP acceptors are able to form a variety of conductive complexes, including the TTF complexes.[1,5,6)] These acceptors, unlike TCNE, are characterized by an effective reduction of the on-site coulombic repulsion, as indicated by a marked decrease in the difference between the first and second reduction potentials. Thus, a reduced on-site coulombic repulsion has been believed to be one of the requisites for organic metals.[4,7)] One may realize that potential electron acceptors are designed by inserting an appropriate conjugated quinonoid system as a building block between two electron-withdrawing dicyanomethylene groups. In this regard, however, it should be noted that the annelated analogues of TCNQ, such as benzo TCNQ,[8)] naphtho TCNQ,[9)] and dibenzo TCNQ,[10)] do not necessarily behave as good electron acceptors, because the annelated groups rather weaken their electron-accepting abilities. In addition, 13,13,14,14-tetracyanodiphenoquinodimethane (TCNDQ), expected to be an electron acceptor with extremely reduced on-site coulombic repulsion, has not been synthesized because of its ready polymerization.[11)] As a part of our efforts toward the development of promising electron acceptors, we have been interested in higher homologues in the extended series of TCNQ and TNAP. In this paper we would like to report on the synthesis and properties of 11,11,12,12-tetracyano-2,6-anthraquinodimethane (abbreviated as TANT) and its 9,

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Present address: Department of Industrial Chemistry, Faculty of Engineering, Kinki University, Higashi-Hiroshima 739-2116, Japan.

10-dichloro derivative (TANT-Cl) as novel electron acceptors with both strong electron affinity and markedly reduced coulombic repulsion.[12)]

The synthesis of TANT was carried out according to Scheme 1. The reduction of commercially available 2,6-diaminoanthraquinone (**1**) with active zinc gave 9,10-dihydroanthracene-2,6-diamine (**2**) in 94% yield, and the subsequent Sandmeyer reaction of **2** was accompanied by dehydrogenation to give 2,6-diiodoanthracene (**3**) in 20% yield. The nucleophilic substitution of **3** with sodium dicyanomethanide in the presence of tetrakis(triphenylphosphine)palladium[13)] gave 2,6-bis(dicyanomethyl)anthracene (**5**) in 65% yield, which was readily dehydrogenated with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) to afford TANT in 98% yield. Alternatively, the chlorination of **3** with chlorine gas gave 9,10-dichloro-2,6-diiodoanthracene (**4**) in 61% yield, which was successfully converted to TANT-Cl by the same procedure.

TANT is a stable, deep-green material, but has the disadvantage of poor solubilities to common solvents. For example, its solubility in dichloromethane is only 6.4×10^{-6} M ($1\ \mathrm{M}=1\ \mathrm{mol\,dm^{-3}}$), which is lower by two or three orders of magnitude than those of TCNQ and TNAP. TANT-Cl also has a similar solubility (5.8×10^{-6} M). The electronic spectrum of TANT is demonstrated together with those of TCNQ and TNAP in Fig. 1, and the absorption maxima are summarized in Table 1. TANT has two intensive absorption bands at 311 and 576.5 nm, of which the latter one is responsible for deep coloration. The marked bathochromic shifts of the long wavelength absorptions in the order of TCNQ, TNAP, and TANT reflect extended quinonoid conjugation in the series. The spectrum of TANT-Cl shows further small bathochromic shifts due to its substituent effect.

The cyclic voltammograms of TANT and TANT-Cl show two reversible redox waves, whose half-wave oxidation potentials are shown together with those of TCNQ and TNAP in Table 1. The first half-wave reduction potential (+0.20 V) of TANT is almost the same as the corresponding ones of TCNQ and TNAP, indicating that TANT is also a strong electron acceptor. The fact that the accepting abilities of TCNQ, TNAP, and TANT are apparently independent of the extension of the central quinonoid system is explained by the result of a balance between a decreasing inductive effect due to separation of the two electron-withdrawing dicyanomethylene groups and an increasing stabilization due to gain of aromaticity of the central quinonoid ring upon reduction.[14)] On the other hand, the second reduction potential (−0.12 V) is much higher than those of TCNQ and TNAP, indicating an effective reduction of the on-site coulombic repulsion, as expected. TANT-Cl bearing the electron-withdrawing chloro substituents has a further stronger accepting ability than does TANT; however, the substituent effect does not affect the difference between the first and second reduction potentials.

The strong electron-accepting abilities of TANT and TANT-Cl allowed the formation of a variety of charge-transfer complexes with electron donors, mostly of the TTT type, as shown in Chart 2.[15)] Complexation with electron donors of the TTF type was generally difficult because of the large solubility difference: an attempted complexation of TANT with TTF, TMTSF, or BEDT-TTF recovered a precipitate

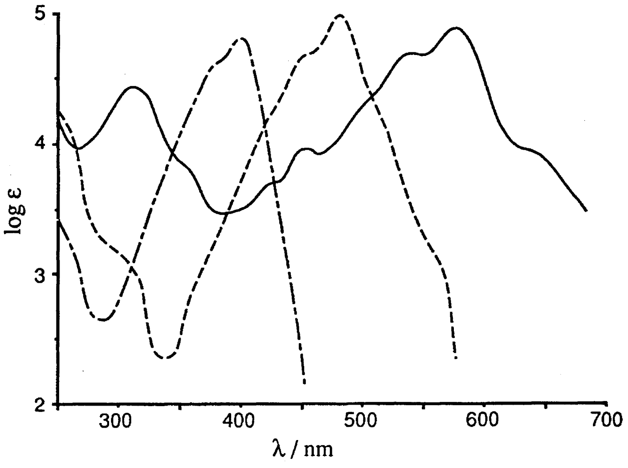
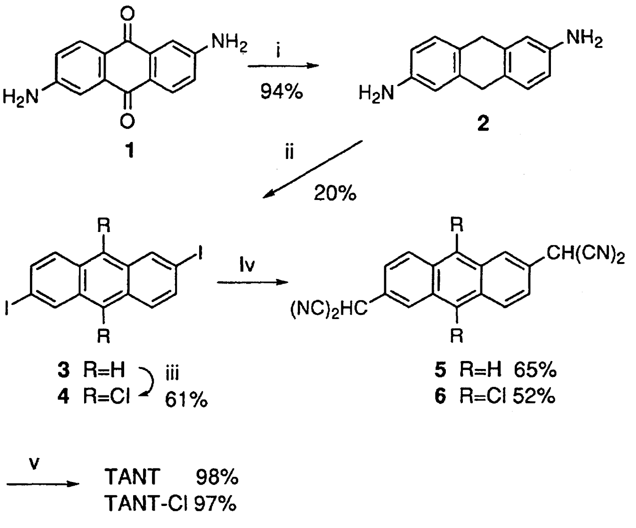


Fig. 1. Electronic spectra of TANT (—), TNAP (- - -), and TCNQ (— — —) in dichloromethane.

Table 1. Electronic Absorption Data[a)] and Half-Wave Reduction Potentials[b)] of TANTs and Related Acceptors

Acceptor	$\lambda_{\max}$/nm (log ε)	$E^1_{1/2}$/V	$E^2_{1/2}$/V	ΔE/V
TANT	311 (4.44), 576.5 (4.89)	+0.20	−0.12	0.32
TANT-Cl	325 (4.34), 586 (4.57)	+0.35	+0.04	0.31
TNAP	479.5 (4.97)	+0.23	−0.21	0.44
TCNQ	400 (4.81)	+0.20	−0.43	0.63

a) Measured in dichloromethane. b) Measured at scan rate 100 mV s^{-1} in benzonitrile containing 0.1 M tetrabutylammonium perchlorate by use of an Ag/AgCl standard electrode and platinum working electrode.



Scheme 1. Reagents and conditions: i) Zn, aq NH_3, 90 °C, 64 h; ii) $NaNO_2$, concd HCl, −3 °C, 10 min, then KI, 100 °C, 1 h; iii) Cl_2, CCl_4, 0 °C, 0.5 h; iv) $Pd(PPh_3)_4$, NaH, $CH_2(CN)_2$, THF, reflux, 20 h, then 10% HCl; v) DDQ, CH_3CN, rt., 1 h.

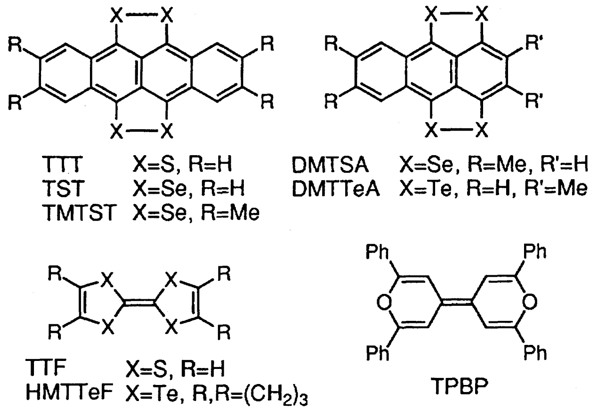


Chart 2.

comprising only the acceptor. However, the stronger electron acceptor TANT-Cl formed a complex with TTF. Their physical properties are summarized in Table 2; all of the thus-obtained complexes have been powdery or fine crystalline, and have had 1 : 1 stoichiometry of the donor and acceptor. Most of the complexes have high conductivities on the order of 10^0—10^1 S cm^{-1}, measured on a compressed pellet. Although there is no essential difference in the conductivity between the TANT complexes and the TANT-Cl complexes, a few complexes with strong electron donors, such as TMTST, DMTTeA, and TPBP, show lower conductivities. It is generally acceptable to assume that conducting charge-transfer complexes have segregated-stacking structures with incomplete charge-transfer. In fact, this explanation is supported by the appearance of an electronic transition at 3100—3700 cm^{-1} for conducting complexes, but no such transition for less conducting ones, as exemplified by the respective solid-state electronic spectra of TANT-TTT and TANT-TMTST in Fig. 2. The low-energy transition is interpreted in terms of electron transfer between the mixed valence species within the stacking columns.[16] In the infrared spectra, the nitrile vibrational absorptions (2185—2195 cm^{-1}) of the conducting complexes are shifted to lower wavenumbers than those of neutral TANT and TANT-Cl (2217 cm^{-1}), also indicating

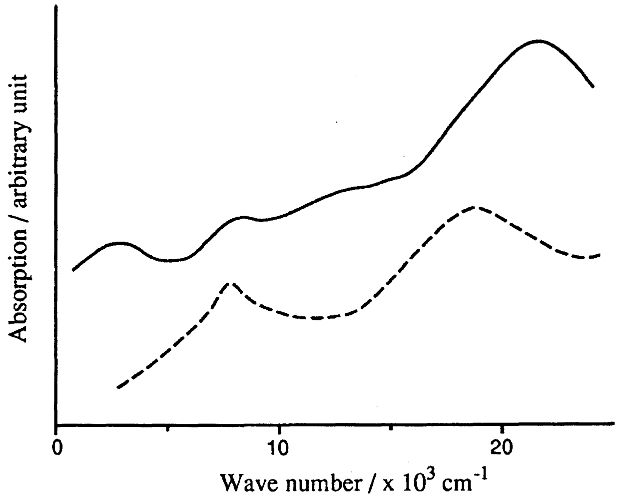


Fig. 2. Electronic spectra of TANT·TTT (—) and TANT·TMTST (- - -) on a KBr disk.

Table 2. Properties of Charge-Transfer Complexes of TANTs with Various Electron Donors

Complex	Appearrance[a,b)]	A : D[c)]	Found (Calcd)[d)]/%			σ[e)]	λ_{max}[f)]	ν_{CN}[f)]
			C	H	N	S cm^{-1}	$\times 10^3$ cm^{-1}	cm^{-1}
TANT·TTT	Deep purple powder	1 : 1	68.94	2.51	8.04	7.0	3.2, 7.2, 10.2	2193, 2179
			(69.49	2.46	8.53)			
TANT·TST	Black powder	1 : 1	54.35	1.97	6.60	6.4	3.2, 7.0	2190
			(54.05	1.91	6.63)			
TANT·TMTST	Black powder	1 : 1	56.08	2.66	6.22	3.4×10^{-2}	6.9	2175
			(56.02	2.69	6.22)			
TANT·DMTSA	Black powder	1 : 1	52.96	2.29	6.76	3.7	3.2, 7.0	2190
			(52.58	2.21	6.81)			
TANT·DMTTeA	Black powder	1 : 1	43.65	1.65	5.24	1.3×10^{-7}	7.1, 10.2	2182, 2153
			(42.52	1.78	5.51)			
TANT·HMTTeF	Deep purple powder	1 : 1	39.75	2.08	5.61	11.5	3.3, 7.1, 12.6	2195
			(39.58	2.08	5.77)			
TANT-Cl·TTT	Deep purple powder	1 : 1	62.75	2.02	7.38	5.9	3.2, 7.0, 10.3	2185
			(62.89	1.94	7.72)			
TANT-Cl·TST	Deep purple powder	1 : 1	50.13	1.56	6.10	8.4×10^{-1}	3.4, 6.8, 9.7	2195
			(49.97	1.54	6.13)			
TANT-Cl·DMTSA	Deep purple powder	1 : 1	48.30	1.86	6.32	2.3	3.1, 6.7, 9.7	2189, 2178
			(48.51	1.81	6.29)			
TANT-Cl·TTF	Deep purple powder	1 : 1	53.59	2.01	9.13	2.3	3.7, 11.6	2192
			(54.07	1.74	9.70)			
TANT-Cl·TPBP	Deep purple needles	1 : 1	76.78	3.70	6.63	4.0×10^{-3}	7.0, 10.0	2187
			(77.42	3.61	6.69)			

a) Prepared in *o*-dichlorobenzene. b) Decomp point > 300 °C. c) Estimated on the basis of elemental analyses. d) Calculated on the basis of the indicated stoichiometry. e) Measured on a compressed pellet at room temperature by the van der Pauw method. f) Measured on a KBr disk.

some charge transfer.[17] On the other hand, the less conducting complexes without an electron transition in the infrared region are supposed to have simple mixed-stacking structures with large charge transfer. The large charge transfer is supported by the appearance of nitrile vibrational absorptions at 2175—2187 cm^{-1}.

In summary, TANT and TANT-Cl are powerful electron acceptors with an effective reduction of the on-site coulombic repulsion, which form a variety of charge-transfer complexes with electron donors mostly of the TTT type. Most of the complexes are highly conducting, and their crystal structures adopt favorable segregated stacking columns with incomplete charge transfer.

Experimental

General Methods: The melting points are uncorrected. All of the chemicals and solvents were of reagent grade. NMR spectra were recorded on a Hitachi R-1200 (60 MHz), a JEOL EX-270 (270 MHz), or a Bruker AMX-400wb (400 MHz) spectrometer in deuteriochloroform with tetramethylsilane as an internal standard. IR spectra were taken on a Hitachi 260-30 spectrometer with a KBr disk. MS spectra were measured at 70 eV on a Shimadzu QP-5000 or a Hitachi-M80B spectrometer using a direct-insertion technique. Electronic spectra were recorded on a Shimadzu UV-3100 spectrometer. Cyclic voltammetry was carried out on a Hokuto Denko HA-301 potentiostat equipped with a Hokuto Denko HB-104 function generator. Conductivity measurements were performed on a compressed pellet by the van der Pauw method with a Fuso Multi-Channel 4-Terminal Conductometer HECS 994.

9,10-Dihydroanthracene-2,6-diamine (2): A stirred mixture of 2,6-diamino-9-10-anthraquinone (**1**) (7.0 g, 29.4 mmol), active zinc (28 g, 428.4 mmol), 28% aqueous ammonia solution (28 mL), and water (14 mL) was heated at 90 °C for 64 h, while an aqueous ammonia solution (100 mL) was added in several parts during the course of the reaction. After being cooled to room temperature, the resulting precipitate was collected by filtration, washed with a small amount of methanol, and dried. It was then thoroughly extracted with acetone (2 L), and the extract was filtered through Celite. Evaporation of the solvent gave a yellow powder of **2**, which was essentially pure and used in the next step without further purification (5.8 g, 94% yield). An analytical sample was obtained as fine yellow crystals by sublimation at 150 °C under 1 Torr (1 Torr = 133.322 Pa); decomp mp 208 °C; IR ν_{NH} 3410 and 3320 cm^{-1}; MS *m/z* 208 (M^+-2); ^{1}H NMR (60 MHz) $\delta = 3.75$ (s, 4H), 6.48 (dd, $J = 7.2$, 1.5 Hz, 2H), 6.61 (d, $J = 1.5$ Hz, 2H), and 7.05 (d, $J = 7.2$ Hz, 2H). Anal. Calcd for $\mathrm{C_{14}H_{14}N_2}$: C, 79.97; H, 6.71; N, 13.32%. Found: C, 79.70; H, 6.51; N, 13.18%.

2,6-Diiodoanthracene (3): Into an ice-cooled mixture of **2** (4.0 g, 19 mmol), ice (10 g), and concd hydrochloric acid (23 mL) was slowly added a solution of sodium nitrite (2.92 g, 42.3 mmol) in water (20 mL) with stirring. After the stirring was continued for 10 min, a solution of potassium iodide (6.4 g, 38.5 mmol) in water (100 mL) was added. The mixture was slowly warmed to room temperature over a period of 1 h, and then heated at 100 °C for 1 h. After being cooled to room temperature, the resulting precipitate was collected by filtration, and washed successively with methanol and dichloromethane. Sublimation at 160 °C under a reduced pressure (5 Torr) followed by recrystallization from chlorobenzene gave gold crystals of **3** (1.65 g, 20% yield): mp > 300 °C; MS *m/z* 430 (M^+); ^{1}H NMR (270 MHz) $\delta = 7.68$ (dd, $J = 9.24$, 1.65 Hz, 2H), 7.73 (d, $J = 9.24$ Hz, 2H), 8.25 (s, 2H), and 8.41 (d, $J = 1.65$ Hz, 2H); Anal. Calcd for $\mathrm{C_{14}H_8I_2}$: C, 39.10; H, 1.87%. Found: C, 39.35; H, 1.81%.

9,10-Dichloro-2,6-diiodoanthracene (4): Into a suspension of **3** (1.57 g, 3.65 mmol) in carbon tetrachloride (250 mL) cooled at 0 °C was bubbled chlorine gas for 30 min; the resulting precipitate was collected by filtration, washed with carbon tetrachloride, and dried. Recrystallization from chlorobenzene gave orange needles of **4** (1.11 g, 61% yield); mp 273—274 °C; MS *m/z* 498 (M^+ based on ^{35}Cl), and 500 (M^++2); ^{1}H NMR (400 MHz) $\delta = 7.86$ (dd, $J = 9.1$, 1.6 Hz, 2H), 8.24 (d, $J = 9.1$ Hz, 2H), and 8.93 (d, $J = 1.6$ Hz, 2H). Anal. Calcd for $\mathrm{C_{14}H_6Cl_2I_2}$: C, 33.70; H, 1.21%. Found: C, 34.02; H, 1.31%.

2,6-Bis(dicyanomethyl)anthracene (5): Into a solution of malononitrile (1.06 g, 16 mmol) in dry THF (60 mL) was added sodium hydride (1.6 g, 40 mmol as 60% oil) in a nitrogen atmosphere; the mixture was stirred for 30 min at room temperature. 2,6-Diiodoanthracene (1.72 g, 4 mmol) and tetrakis(triphenylphosphine)palladium(0) (960 mg, 0.8 mmol) were added, and the mixture was refluxed for 20 h. After being cooled to room temperature, the reaction mixture was treated with 10% hydrochloric acid (3 mL), and the solvent (THF) was evaporated. The residue was acidified by the further addition of 10% hydrochloric acid; the resulting solid was collected by filtration, and washed successively with water, ethanol, and chloroform. Recrystallization from acetonitrile gave yellow prisms of **5** (793 mg, 65% yield): mp > 300 °C; ^{1}H NMR (400 MHz, acetone-d_6) $\delta = 6.30$ (s, 2H), 7.75 (d, $J = 9.0$ Hz, 2H), 8.35 (d, $J = 9.0$ Hz, 2H), 8.34 (s, 2H), and 8.85 (s, 2H); IR ν_{CN} 2262 cm^{-1}; MS *m/z* 306 (M^+). Anal. Calcd for $\mathrm{C_{20}H_{10}N_4}$: C, 78.42; H, 3.29; N, 18.26%. Found: C, 78.21; H, 3.14; N, 18.26%.

2,6-Bis(dicyanomethyl)-9,10-dichloroanthracene (6): Compound **6** was prepared in 52% yield from **4** in a manner similar to that described for **5**: yellow needles from acetonitrile; mp (decomp) 278—279 °C; MS *m/z* 374 (M^+ based on ^{35}Cl) and 376 (M^++2); ^{1}H NMR (400 MHz, acetone-d_6) $\delta = 8.80$ (s, 2H), 8.70 (d, $J = 9.2$ Hz, 2H), 7.96 (d, $J = 9.2$ Hz, 2H), and 6.38 (s, 2H); IR ν_{CN} 2260 cm^{-1}. Anal. Calcd for $\mathrm{C_{20}H_8N_4Cl_2}$: C, 64.02; H, 2.15; N, 14.93%. Found: C, 63.91; H, 2.15; N, 14.73%.

11,11,12,12-Tetracyano-2,6-anthraquinodimethane (TANT): Compound **5** (200 mg, 0.652 mmol) was thoroughly dissolved in acetonitrile (120 mL) under reflux in a nitrogen atmosphere and allowed to cool to room temperature. A solution of DDQ (444 mg, 1.96 mmol) in acetonitrile (20 mL) was added, and the mixture was stirred for 1 h. The resulting solid was collected by filtration and washed with acetonitrile and then dichloromethane to leave a deep green powder of TANT (195.8 mg, 98% yield): mp > 300 °C; IR ν_{CN} 2217 and 2208 cm^{-1}; high-resolution MS *m/z* 304.0752 (M^+). Calcd for $\mathrm{C_{20}H_8N_4}$: M, 304.0749. Anal. Calcd for $\mathrm{C_{20}H_8N_4}$: C, 78.94; H, 2.65; N, 18.41%. Found: C, 78.70; H, 2.60; N, 18.27%. The thus-obtained TANT powder was analytically pure, and its recrystallization was difficult because of poor solubility and gradual decomposition in a hot solution.

9,10-Dichloro-11,11,12,12-tetracyano-2,6-anthraquinodimethane (TANT-Cl): TANT-Cl was obtained in 97% yield from **6** in a similar manner as described for the preparation of TANT; deep green powder; mp > 300 °C MS *m/z* 372 (M^+ based on ^{35}Cl) and 374 (M^++2); IR ν_{CN} 2217 cm^{-1}. Anal. Calcd for $\mathrm{C_{20}H_6N_4Cl_2}$: C, 64.37; H, 1.62; N, 15.01%. Found: C, 64.40; H, 1.64; N, 14.73%.

Complexation: All charge-transfer complexes described in this report were prepared by mixing two hot saturated solutions of donor and acceptor in *o*-dichlorobenzene in a nitrogen atmosphere. The complexes precipitated out upon cooling were collected by filtration and dried.

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