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Tetracyanoanthraquinodimethanes with a Chiral Amide Group: Preparation, Properties, and Charge-Transfer Photochirogenetic Reaction with 1,2-Dianisylacenaphthene-1,2-diol†

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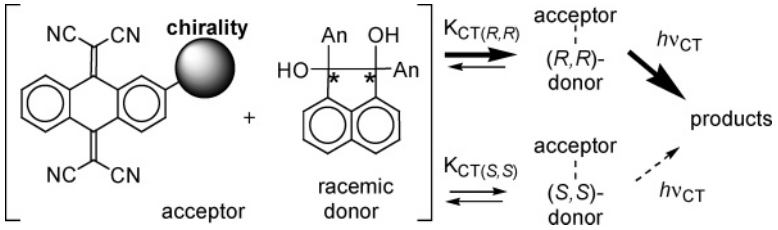

A series of butterfly-shaped tetracyanoanthraquinodimethanes (TCNAQs) with a chiral amide auxiliary **1a**−**f** were prepared from the corresponding anthraquinones. They are stronger acceptors than the unsubstituted derivative and undergo one-wave two-electron reduction. They form weak electron-donor-acceptor (EDA) complexes with the title pinacol **2**. Upon charge-transfer excitation of these complexes, dihydro-TCNAQs **3** and 1,8-dianisoylnaphthalene **4** were efficiently formed, the latter of which is the product of a retropinacol reaction via $\mathbf{2}^{+\bullet}$. Partial enantiodifferentiation of *rac*-**2** was realized during the photoreactions with 2-[(*R*)-1-phenylethylcarbamoyl]-TCNAQ **1a** in CD_3CN. Thus, optically active (*S,S*)-(+)-pinacol **2** (12.3% ee at 54% conversion; 21.5% ee at 70% conversion) was recovered from the photolyzates. This reaction represents a new and rare example of the pseudokinetic resolution of *tert*-alcohol accompanied by C−C bond fission. Significant differences in the association constants for the diastereomeric EDA complexes are responsible for the observed enantiodifferentiation.

11,11,12,12-Tetracyano-9,10-anthraquinodimethane (TCNAQ) is the dibenzo analogue of 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ), the latter of which is a well-known electron acceptor that gives a plethora of electroconducting organic solids. A representative example is the crystalline charge-transfer (CT) complex with tetrathiafulvalene (TTF), and research on organic conductors was initiated by the discovery of this first molecular metal.[1] Although TTF[2] and its selenium analogue[3] have often been used to provide strong donating properties for more sophisticated molecules, easy deformation of the TCNQ skeleton prevents the modified acceptors from inheriting the intrinsic redox behavior.[4] This is also the case with TCNAQ, which is calculated to be a much weaker acceptor as a result of the severely deformed butterfly-shaped molecular geometry.[5]

The preparation of TCNAQ was first reported by Misumi's group.[6] Soon thereafter, Hünig and co-workers succeeded in the direct conversion of anthraquinones to TCNAQs[7] by condensation reactions with malononitrile

† Dedicated to Prof. Tsutomu Miyashi on the occasion of his 65th birthday.

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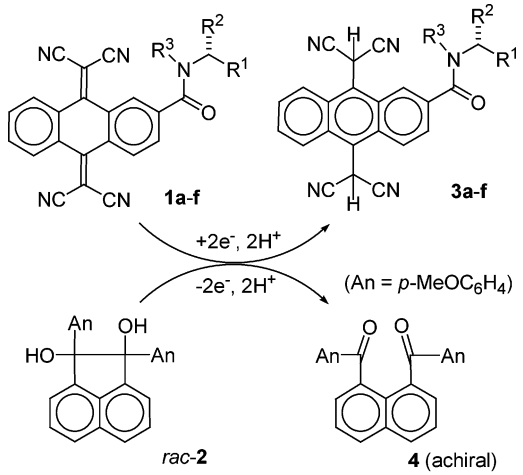
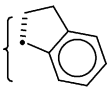
in the presence of $TiCl_4$.[8] Their detailed studies on redox behavior revealed that TCNAQs undergo successive two-electron capture nearly at the same potential[7,9] which can be accounted for by a drastic structural change upon reduction.[10] After these pioneering works, several groups, including us, succeeded in preparing TCNAQs by different methods,[11−13] yet the $TiCl_4$-assisted preparation is the most versatile for obtaining a wide variety of functionalized materials based on the TCNAQ skeleton,[14] including the intramolecular donor−acceptor compounds,[15] photoconducting polymers,[16] EL devices,[17] and LB films.[18]

In addition to these examples, we recently found that TCNAQs with a chiral ester group can serve as an unprecedented molecular response system, by which an electrochemical input is transduced into three-way spectral outputs (UV−vis, fluorescence, and circular dichroism).[19] Although only a limited number of chiral electron acceptors have been reported to date,[20] we believe that they may constitute an important class of compounds for the development of novel materials such as electrochiroptical,[21] mesophase,[22] and NLO devices.[23] In our continuing studies on chiral redox systems, we have found that the newly designed TCNAQs **1** with a chiral amide auxiliary can act as stereodifferentiating oxidants under CT excitation conditions. In the first portion of this paper, we report the preparation, redox properties, and X-ray structures of the title acceptors **1**. In the second part, we show the photochemical reactions of TCNAQs **1** with *rac*-1,2-dianisylacenaphthene-1,2-diol **2** that give the dihydro-TCNAQs **3** and achiral 1,8-dianisoylnaphthalene **4** (Scheme 1). Racemic pinacol **2** was partially deracemized by **1** upon irradiation and thus provides a new entry into the less well-developed subject of photochirogenesis[24] under photoinduced electron-transfer (PET) conditions.[25,26]

SCHEME 1. Photoinduced Electron-Transfer Reactions of TCNAQs 1 and Pinacol 2



	a	b	c	d	e	f
R^1	Ph	Ph	Ph		Ph	*c*Hex
R^2	Me	Et	*i*Pr		Me	Me
R^3	H	H	H	H	Me	H

Results and Discussion

1. TCNAQs 1a−f with a Chiral Amide Auxiliary. Preparation and Redox Properties. α-Substituted benzylamines are easily accessible asymmetric molecules,[27] and the benzylcarbamoyl-TCNAQs **1a−f** were

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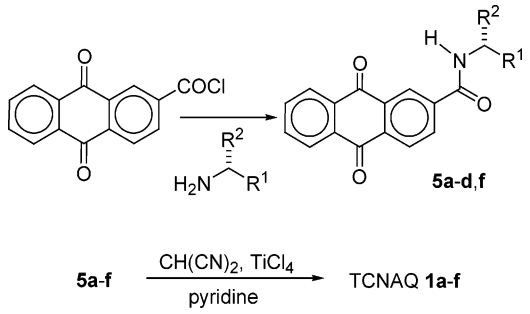
SCHEME 2. Preparation of Chiral TCNAQs 1



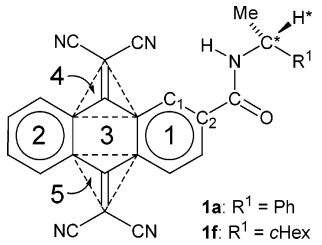
designed so as to incorporate these asymmetric centers with an (*R*)-configuration. To avoid unnecessary steric repulsion between the dicyanomethylene group and the amide moiety, the chiral substituents are attached at the 2-position of TCNAQ (Scheme 2). The corresponding anthraquinones **5a**−**f** were selected as precursors and prepared in yields of 62−98% by the reactions of anthraquinone-2-carbonyl chloride with chiral amines except for *tert*-amide **5e**, which was more conveniently prepared by *N*-methylation of **5a** in quantitative yield.

Although 1-phenylethyl anthraquinone-2-carboxylate could not be converted into the corresponding TCNAQ[28] under the standard conditions ($TiCl_4$/pyridine), the reaction of phenylethylamide **5a** with malononitrile proceeded smoothly to give 2-[(*R*)-1-phenylethylcarbamoyl]-TCNAQ **1a** in 61% yield. Similarly, **1b**−**f** were obtained from the corresponding quinones **5b**−**f** in respective yields of 41−97%. The newly prepared TCNAQs are stable crystalline materials and were purified by chromatography and/or recrystallization.

In contrast to that for the anthraquinone precursor **5a** ($E_1^{red} = -0.85$ V, $E_2^{red} = -1.31$ V vs SCE), the cyclic voltammogram of TCNAQ **1a** in MeCN shows only one pair of reversible redox waves ($E^{red} = -0.32$ V). Similarly, other derivatives **1b**−**f** undergo one-wave two-electron reduction at a similar potential (−0.32 to −0.34 V), showing that all of the newly prepared TCNAQs inherit the intrinsic redox behavior of the parent TCNAQ.[7,11,12] The slightly positive values of E^{red} compared to that for the unsubstituted TCNAQ (−0.37 V) can be explained by the electron-withdrawing ability of the carbamoyl group, which is hardly affected by the difference in the steric requirements of the chiral centers.

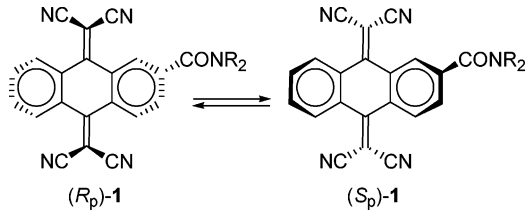
Molecular and Crystal Structures. X-ray structural analyses of (*R*)-phenylethylamide **1a** and (*R*)-cyclohexylethylamide **1f** have shown that the TCNAQ skeleton in them adopts a severely deformed butterfly-shaped geometry, as observed in the unsubstituted TCNAQ.[31] Selected dihedral angles for the two crystallographically independent molecules of **1a** (mol-1 and mol-2) and those for **1f** are listed in Table 1. Although all molecules of **1f** in a crystal adopt a planar chirality of (*S*) (Figure S3), this may not be due to direct control by the chiral center of the amide side chain but rather could arise from crystal packing effects. In fact, a crystal of **1a** contains both diastereomers [(*R*)- and (*S*)-configuration of planar chirality] in a 1:1 ratio (Figures S1 and S2). The NMR spectra of **1a** and **1f** with sharp resonances suggest that the butterfly-shaped geometry is freely inverted in solution (Scheme 3) and fixed to the planar chirality of (*R*) or (*S*) upon crystallization, and this preference is mainly determined by the crystal packing force.

TABLE 1. Selected Geometrical Parameters of 1a and 1f Determined by X-ray Analyses



	1a (mol-1)	**1a** (mol-2)	**1f**
dihedral angle (deg) between			
planes 1 and 2	143.4	138.0	135.9
planes 3 and 4	31.0	29.9	34.5
planes 3 and 5	30.0	29.7	31.8
torsion angle (deg) around			
$C_1-C_2-C_{CO}-O_{CO}$	11.5	147.7	143.1
$O_{CO}-C_{CO}-N_{NH}-H_{NH}$	169.8	177.7	175.2
$H_{NH}-N_{NH}-C^*-H^*$	164.0	136.2	176.7

SCHEME 3. Planar Chirality of Interconvertible (*R*)- and (*S*)-TCNAQ



The torsion angles around the amide moieties of **1a** and **1f** exhibit considerable variation (Table 1), which reflects the rotational and conformational flexibility of the chiral side chain. A common feature observed in these solid-state structures is the *trans*-conformation of the -CONH- group (torsion angle 169.8−177.7°), which is in accord with the preference reported for a series of aromatic secondary amides.[32]

In a crystal of cyclohexylethylamide **1f**, molecules are connected by intermolecular CO···HN hydrogen bonds (O···H, 1.99 Å; O···N, 2.92 Å; O···H−N, 165.9°) to form an infinite network along the *a* axis (Figure 1). In this one-dimensional array, the cyclohexyl moiety of a certain

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(28) Consistent with the facile nucleophilic transformation of the dicyanomethylene group (ref 29), TCNAQs are prone to be hydrolyzed under alkaline conditions to reproduce anthraquinones (ref 12a). This is the major reason their condensations with malononitrile do not proceed in the absence of $TiCl_4$. When this Lewis acid induces the degradation of substrates as in the case of this phenylethyl ester, other conditions such as dry pyridine/MS4A (refs 12a, 30) seem promising. With this method, we could prepare 2-[(*R*)-1-phenylethylcarbonyloxy]-TCNAQ (**1i**), which cannot be obtained by the protocol using $TiCl_4$.

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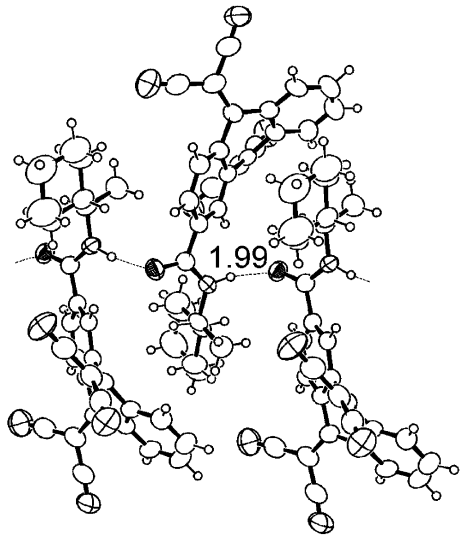

FIGURE 1. Molecular arrangement in the crystal of **1f** determined by the X-ray analysis. Short CO···NH contacts are shown by broken lines.

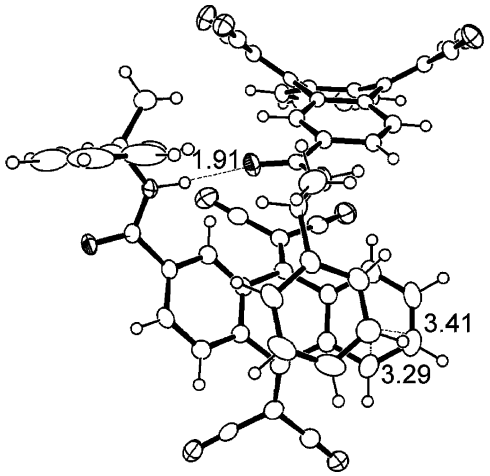

FIGURE 2. Molecular arrangement in the crystal of **1a** determined by the X-ray analysis. Short CO···NH and C···C ($\pi-\pi$) contacts are shown by broken lines.

molecule is accommodated in the butterfly-shaped cavity made by the neighboring TCNAQ. In the case of **1a**, the crystal structure composed of two crystallographically independent molecules is more complicated but shares some common features with **1f**. There is a hydrogen bond between CO in mol-1 and HN in mol-2 (1.91 Å, 2.89 Å, 168.2°) to form a dyad (Figure 2), where the phenyl group of mol-1 is deeply included in the cavity of mol-2 with a face-to-face π overlap[33] and van der Waals contacts of C···C (3.29 and 3.41 Å). The dyad of **1a** is further connected along the *b* axis by another hydrogen bond (2.02 Å, 2.96 Å, 162.4°) to form an infinite lattice.

The hydrogen-bonded network is a common structural motif observed in crystals of **1a** and **1f**, which may be related to the geometrical variations about the amide auxiliary in the solid-state molecular structures. The accommodation of a phenyl or cyclohexyl group in the butterfly-shaped cavity of the neighboring TCNAQ skeleton is another common feature. Such inclusion behavior was previously observed when we carried out X-ray analyses[34] on crystalline CT complexes of TCNAQs.[35] These results prompted us to explore CT complexation of chiral TCNAQs **1** with *rac*-1,2-dianisylacenaphthene-1,2-diol **2**. We anticipated that the electron-donating naphthalene nucleus or one of the anisyl groups of **2** would be incorporated in the electron-deficient cavity of **1**, and hydrogen bonds between the CO of **1** and HO of **2** may enhance the association.[36] It would be of special interest to clarify if **1** with a chiral amide group could differentiate enantiomers of pinacol **2** to result in the diastereoselective formation[37a] of electron-donor−acceptor (EDA) complexes in solution.[38] We envisaged that the diastereoselectivity, if any, could be evaluated through the photoreaction of the EDA complexes, where **1** could serve as a chiral oxidant toward **2**. The results will be shown in the next section.

2. CT Excitation Reaction of TCNAQs 1a−f and Pinacol 2.

Photoreaction of TCNAQ and Pinacol. Excitation of the CT absorption band (CT excitation) is one of the two common protocols in photoinduced electron transfer (PET) reactions. Although the photosensitized reaction is generally a more effective alternative in terms of quantum yield,[39] the close proximity of the radical ions that result from CT excitation is preferable from the viewpoint of stereodifferentiation by the chiral auxiliary of **1**. The TCNAQ skeleton is of special interest in PET reactions[40] since the change in geometry upon electron capture retards back electron-transfer (BET), which suppresses the main cause of the ineffectiveness of the reaction in the CT excitation protocol. In fact, we previously found[41] that 2,6-dibromo-substituted TCNAQ **1h** acts as a strong oxidant under photoirradiation conditions to induce the retropinacol reaction[39,42] of 1,2-diarylacenaphthene-1,2-diols such as **2**. In these reactions, the acceptor was converted to a 2,6-dibromo

(33) Crystalline **1a** exhibits a yellow color, whereas **1f** is nearly colorless. Weak CT interaction through a face-to-face π overlap in the former can explain this difference.

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(35) Mukai, T.; Suzuki, T.; Yamashita, Y. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2433.

(36) When *rac*-pinacol **2** was recrystallized from EtOH, the EtOH-solvated crystal was obtained. X-ray analysis showed that the hydroxy groups of **2** are involved in hydrogen bonds with the solvent. Similarly, hydrogen bonds between **2** and solvent are present in the EtOH solvate of optically pure (*S,S*)-**2**.

(37) (a) Both CT interaction and hydrogen bonds are considered to be important factors for obtaining high diastereoselectivity upon the separation of enantiomers by chiral HPLC: Perkle, W. H.; Pochapsky, T. C. *J. Am. Chem. Soc.* **1987**, *109*, 5975. Perkle, W. H.; Pochapsky, T. C.; Mahler, G. S.; Corey, D. E.; Reno, D. S. *J. Org. Chem*. **1986**, *51*, 4991. Perkle, W. H.; Welch, C. J. *Tetrahedron: Asymmetry* **1994**, *5*, 777. (b) In the present case, diastereoselectivities caused by CT interaction and hydrogen bonds would be mismatched to induce lower selectivity in less polar $CDCl_3$.

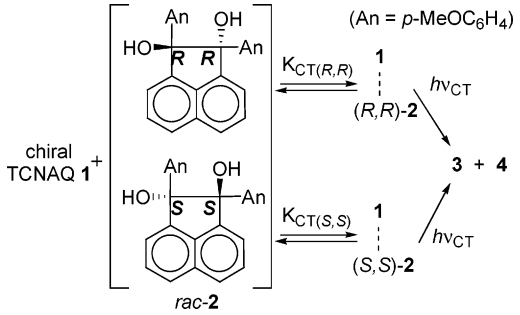
(38) Many attempts to isolate crystalline complexes were unsuccessful.

(39) Perrier, S.; Sankararaman, S.; Kochi, J. K. *J. Chem. Soc., Perkin Trans. 2* **1993**, 825.

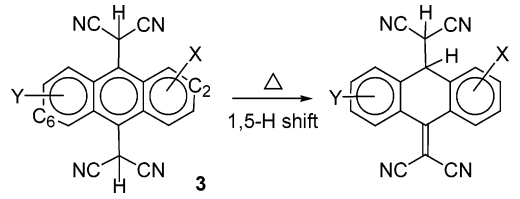
(40) (a) Janssen, R. A. J.; Christiaans, M. P. T.; Hare, C.; Martín, N.; Sariciftci, N. S.; Heeger, A. J.; Wudl, F. *J. Chem. Phys.* **1995**, *103*, 8840. (b) Imahori, H.; Hasegawa, M.; Taniguchi, S.; Aoki, M.; Okada, T.; Sakata, Y. *Chem. Lett.* **1998**, 721. (c) Zerza, G.; Scharber, M. C.; Brabec, C. J. Sariciftci, N. S.; Gomez, R.; Segura, J. L.; Martín, N.; Srdanov, V. I. *J. Phys. Chem. A* **2000**, *104*, 8315. (d) Zerza, G.; Cravino, A.; Neugebauer, H.; Sariciftci, N. S.; Gómez, R.; Segura, J. L.; Martín, N.; Svensson, M.; Andersson, M. R. *J. Phys. Chem. A* **2001**, *105*, 4172. (e) Donkers, R L.; Workentin, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 1688.

(41) Miyashi, T.; Suzuki, T. *Kokagaku* **1990**, *14,* 42.

SCHEME 4. EDA Complexation between 1 and Enantiomers of 2



SCHEME 5. Thermal Isomerization of Dihydro-TCNAQ 3



derivative of 9,10-bis(dicyanomethyl)anthracene (dihydro-TCNAQ, **3**),[43] whereas the pinacols were transformed into the corresponding 1,8-diaroylnaphthalenes via a facile mesolytic bond fragment[44] of pinacol cation radicals. With these results in mind, we designed here a novel asymmetric photochemistry based on the preferential formation of diastereomeric EDA complexes between chiral TCNAQ **1** and (*R,R*)- or (*S,S*)-**2** in solution (Scheme 4).[45] Although both enantiomers of **2** are transformed into achiral diketone **4**, the recovered pinacol **2** would become optically active when photoirradiation is stopped before the reactions are complete. This study should provide an unprecedented technique for the pseudo-kinetic resolution of pinacols under photochemical conditions.

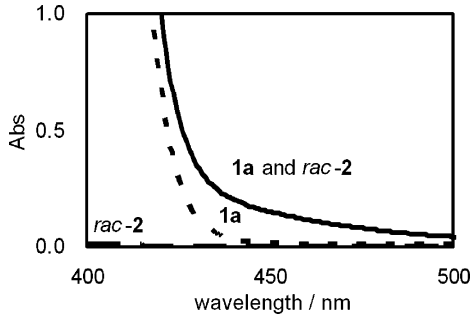


FIGURE 3. UV-vis absorption of **1a** (2×10^{-2} mol dm^{-3}), *rac*-**2** (2×10^{-2} mol dm^{-3}), and their mixture (2×10^{-2} mol dm^{-3} each) in CH_3CN.

Enantiodifferentiating Photoreaction of TCNAQ 1a and *rac*-2. Upon the admixture of 2-[(*R*)-1-phenylethylcarbamoyl]-TCNAQ **1a** (2×10^{-2} mol dm^{-3}) and *rac*-**2** (2×10^{-2} mol dm^{-3}) in CH_3CN, a new absorption band appeared in the visible region, which was assigned to the CT band from the pinacol donor **2** ($E^{ox} = +1.24$ V) to **1a** (Figure 3). The association constant ($K_{CT(rac)}$) was determined to be 2.9 mol^{-1} dm^3 by using the Benesi–Hildebrand equation[46] at 23 °C. Significantly different values were obtained upon complexation of **1a** with enantiomers of **2**: $K_{CT} = 4.5$ mol^{-1} dm^3 for (*R,R*)-(−)-**2** and 1.6 mol^{-1} dm^3 for (*S,S*)-(+)-**2**. Therefore, the CT excitation reaction between **1a** and *rac*-**2** may consume (*R,R*)-(−)-**2** faster than (*S,S*)-(+)-**2** in CH_3CN. To excite the EDA complex selectively, the irradiation wavelength is adjusted to $\lambda > 435$ nm by using a glass cutoff filter in the subsequent photoreactions.

Upon irradiation of a 0.6 mL CD_3CN solution of TCNAQ **1a** and *rac*-pinacol **2** (2×10^{-2} mol dm^{-3} each) by a 500-W Xe lamp at 0 °C, **1a** and **2** were consumed gradually with the concomitant formation of dihydro-TCNAQ **3a**[43b] and diketone **4**. No other species were observed in the ^{1}H NMR spectra of the reaction mixtures, which shows that the retropinacol reaction under PET conditions proceeded smoothly as in the case of dibromo-TCNAQ **1h**.[41] Nearly half of the pinacol **2** was consumed within 1 h on the basis of ^{1}H NMR analyses, and the reaction mixture was separated using SiO_2 TLC followed by HPLC. Only negligible amounts of **1a**, **2**, and **4** were lost during the separation.[43b] To confirm that the photoreaction of chiral TCNAQ **1a** and the enantiomers of **2** proceeds with a difference in efficiency, the enantiomeric excess (ee) of the recovered **2** was determined by chiral HPLC, which gave a value of 12.3% ee [rich in (*S,S*)-(+)-**2**][47] at 54% conversion. Nearly identical values were obtained in two additional runs of similar experiments. A higher value of 21.5% ee was obtained at 70% conversion upon prolonged irradiation (3 h) in CD_3CN. Although the observed enantiodifferentiation is far from perfect,

(42) (a) Reichel, L. W.; Griffin, G. W.; Muller, A. J.; Das, P. K.; Ege, S. N. *Can. J. Chem.* **1984**, *62*, 424. (b) Sankararaman, S,; Kochi, J. K. *J. Chem. Soc., Chem. Commun.* **1989**, 1800. (c) Zhang, W.; Yang, L.; Wu, L.-M.; Liu, Y.-C.; Liu, Z.-L. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1189. (d) Gan, H.; Leinhos, U.; Gould, I. R.; Whitten, D. G. *J. Phys. Chem.* **1995**, *99*, 3566.

(43) (a) Very low solubility and strong C−H acidity hampered full characterization of the dibromo derivative of dihydro-TCNAQ **3h**. Another obstacle is its easy isomerization to 2,6-dibromo-9,10-dihydro-9-dicyanomethyl-10-dicyanomethyleneanthracene by a thermal 1,5-H shift (Scheme 5), which is facilitated by polar solvents in which **3h** can be dissolved. (b) Because of difficulties similar to those with dibromide **3h**, dihydro-TCNAQs **3a**−**f** with an amide side chain could not be isolated or fully characterized. We confirmed their formation and quantity based on the ^{1}H NMR analyses of the reaction mixtures. Although **3a**−**f** are more soluble than **3h**, the pale yellow color of **3a**−**f** turned deep violet upon contact with SiO_2, which is characteristic of the dianionic species of TCNAQs $\mathbf{1}^{2-}$ (ref 19). The anionic dyes were strongly adsorbed on SiO_2 and were difficult to elute before air oxidation of $\mathbf{1}^{2-}$ to **1**.

(44) Maslak, P.; Chapman, W. H., Jr.; Narvaez, J. N.; Vallombroso, T. M., Jr.; Watson, B. A. *J. Am. Chem.* Soc. **1995**, *117*, 12380.

(45) Besides the difference in the association constants ($K_{CT(R,R)}$ vs $K_{CT(S,S)}$), two other factors may contribute to the deracemization of **2**. One is the difference in the reaction rates (k_1) from the radical ion pairs ($\mathbf{1}^{-\bullet}/\mathbf{2}^{+\bullet}$) to the products (**3** and **4**), and the other is the difference in the rates for BET (k_2). The former reaction consists of very facile intramolecular processes such as conformational change of $\mathbf{1}^{-\bullet}$ (ref 7−12) or C−C bond cleavage of $\mathbf{2}^{+\bullet}$ (refs 39, 42), so that the relative orientation of radical ions would not greatly affect the rate ($k_{1(R,R)} = k_{1(S,S)}$). Since electrons can transfer from one to another over a considerable distance, there is only a slight chance that the rates of BET differ in the diastereomeric contact ion pairs ($k_{2(R,R)} = k_{2(S,S)}$). From the above points of view, the enantiodifferentiation observed in the present work can be ascribed mainly to the preferential formation of diastereomeric EDA complexes.

(46) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1960**, *82*, 2134.

(47) The optical resolution of sterically hindered *tert*-alcohols is a difficult task. The first successful nonenzymatic kinetic resolution was reported only very recently (ref 48). This is also the case for *rac*-pinacol **2**, which had not been resolved before. There was no information about the chiroptical properties or absolute configurations of the enantiomers. The optical resolution procedures for **2** are given in Supporting Information.

TABLE 2. Conversion Ratio of Pinacol 2 and Enantiomeric Excess[a] of Recovered 2 after Irradiation[b] of EDA Complexes Consisting of TCNAQ 1a−f and *rac*-2

(*R*)-$R^1R^2C^*H$-NR^3-CO- group of **1**	**a**	**b**	**c**	**d**	**e**	**f**
R^1	Ph	Ph	Ph	*c*	Ph	*c*Hex
R^2	Me	Et	*i*Pr	*c*	Me	Me
R^3	H	H	H	H	Me	H
in CD_3CN						
conv (%)	54	48	48	55	51	*d*
ee (%)	+12.3	+12.2	+11.5	−0.6	+0.8	
in $CDCl_3$						
conv (%)	56	50	50	52	50	49
ee (%)	+2.7	+1.4	+1.6	+0.8	<0.5	+2.3

[a] Values with a plus sign indicate that the recovered **2** is rich in (*S,S*)-(+)-**2**. [b] Irradiated by a 500-W Xe lamp through a glass cutoff filter (λ > 435 nm) at 0 °C. [**1**] = [*rac*-**2**] = 2×10^{-2} mol dm^{-3}. Irradiation time is 1 h (**a**−**g** in CD_3CN), 2 h (**a**, **d**, **e** in $CDCl_3$), 2.5 h (**c** in $CDCl_3$), or 2.7 h (**b** in $CDCl_3$). [c] (1*R*)-Indanyl. [d] Because of the low solubility, the reaction could not be conducted under comparable conditions.

this reaction provides a new and rare example of asymmetric photoreactions under CT excitation conditions.[25,49]

When the photoreactions of **1a** and *rac*-**2** were conducted in $CDCl_3$, **2** was converted to **4** more slowly than in CD_3CN. After irradiation for 2 h, 56% of pinacol **2** was consumed, and the enriched (+)-**2** that was recovered exhibited only marginal optical purity (2.7% ee determined by both chiral HPLC and CD spectrum). The much lower enantiodifferentiation attained in $CDCl_3$ is consistent with the fact that the K_{CT} values of **1a** with enantiomers of **2** are nearly the same in $CHCl_3$: $K_{CT(R,R)}$ = 0.9 mol^{-1} dm^3; $K_{CT(S,S)}$ = 1.3 mol^{-1} dm^3. Comparisons of K_{CT} values in $CHCl_3$ and CH_3CN suggest that the hydrogen bonds between **1a** and **2** in the former solvent, if any, do not enhance the association or increase the enantiodifferentiation.[37b] To further investigate the observed solvent effects as well as the stereogenic effects of chiral centers, CT excitation reactions of EDA complexes were carried out for other combinations of TCNAQ **1b**−**f** with **2**.

Enantiodifferentiating Photoreactions of TCNAQ 1b−f and *rac*-2. When EDA complexes composed of **1b**−**f** and *rac*-**2** were irradiated with a 500-W Xe lamp through a glass cutoff filter (λ > 435 nm) at 0 °C, nearly half of the pinacol **2** was consumed within 1 h in CD_3CN and within 2−2.7 h in $CDCl_3$. The recovered pinacol **2** was enriched with the (*S,S*)-(+)-enantiomer in all cases except one (**1d** in CD_3CN), which shows that the stereogenic effects of chiral benzylcarbamoyl groups with (*R*)-configuration endow **1** with a diastereomeric preference for (*R,R*)-(−)-**2** upon EDA complexation. On the other hand, the degree of this preference differs considerably depending on the steric requirements of chiral centers, as shown in Table 2.

(*R*)-Phenylpropylamide **1b** (R^1 = Ph, R^2 = Et) and (*R*)-phenylisobutylamide **1c** (R^1 = Ph, R^2 = *i*Pr) exhibit a similar degree of enantiodifferentiation as **1a** (R^1 = Ph, R^2 = Me), and pinacol **2** was recovered with an optical purity of more than 10% ee at 48% conversion when the photoreactions were carried out in CD_3CN. The optical purity decreased drastically when the photoreactions of **1b** and **1c** were conducted in $CDCl_3$, which is consistent with the solvent effects observed for **1a**. On the other hand, neither bicyclic amide **1d** nor *tert*-amide **1e** induced more than 1% ee for the recovered pinacol **2**. Since aromatic tertiary amides prefer a geometry different from that of the secondary ones,[32] the loss of stereoselectivity may be related to such a drastic geometrical difference around the chiral amide group. This may also be the case for **1d**, which has a stereogenic center confined in a ring structure. Notably, the aromatic ring is not essential at the asymmetric center since alicyclic amide **1f** (R^1 = *c*Hex, R^2 = Me) induced a similar optical purity for **2** as **1a**−**c** in $CDCl_3$. This suggests that the π-type substituent at the chiral center plays only a slight role in the diastereoselective complexation of **1** with (*R,R*)-(−)-**2**. A secondary amide group with a large difference in steric demand between R^1 and R^2 should be a promising chiral auxiliary for attaining a higher enantiodifferentiation of pinacol **2**.[50]

Conclusion

In this work, we prepared a series of TCNAQs **1** with a chiral benzylcarbamoyl auxiliary, which act as strong oxidants to induce the retropinacol reaction of **2** upon the photoirradiation of EDA complexes. Although the asymmetric centers of **1** do not strongly affect the planar chirality of the TCNAQ skeleton or the conformations of chiral side chains in the solid state, some of them play an important role in realizing the partial deracemization of **2** through the pseudo-kinetic resolution of sterically hindered *tert*-alcohol[47] in solution. This reaction can serve as a novel prototype of photochirogenesis using the CT excitation protocol.[51]

Experimental Section

Preparation of TCNAQs 1a−f. To a solution of 2-[(*R*)-1-phenylethylcarbamoyl]anthraquinone **5a** (1.42 g, 4.00 mmol) and malononitrile (1.32 g, 20.0 mmol) in dry $CHCl_3$ was added $TiCl_4$ (8.00 mL, 72.0 mmol) followed by dry pyridine (16 mL) dropwise over 10 min at 0 °C. After the mixture was refluxed for 8 min, the solvent was removed under reduced pressure. The residue was treated with aqueous HCl (6 mol dm^{-3}, 200 mL) and extracted with $CHCl_3$. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration and removal of solvent, the residue was chromatographed on SiO_2 and further purified by recrystallization from CH_3CN to give 11,11,12,12-tetracyano-2-[(*R*)-1-phenylethylcarbamoyl]-9,10-anthraquinodimethane **1a** (1.09 g) as yellow needles in 61% yield. Other TCNAQs **1b**−**f** were similarly prepared by start-

(48) Nishimura, T.; Matsumura, S.; Maeda, Y.; Uemura, S. *Tetrahedron Lett.* **2002**, *43*, 3037.

(49) Suzuki, T.; Fukushima, T.; Yamashita, Y.; Miyashi, T. *J. Am. Chem. Soc.* **1994**, *116*, 2793.

(50) (a) According to this idea, 2-[(*R*)-1-(2-naphthyl)ethyl]-TCNAQ (R^1 = 1-naphthyl, R^2 = Me) (**1j**) was prepared, yet very low solubility in common solvents hampered its use in photoreactions. (b) A preliminary study showed that a C_2-symmetric TCNAQ derivative with two (*R*)-phenylethylamide groups at 2,6-positions (**1k**) could also be used for an enantiodifferentiating photoreaction, yet the recovered **2** exhibited a similar degree (10.7% ee at 52% conversion by 0.5 h of irradiation in CD_3CN at 0 °C) of optical activity as with **1a**, which has only one chiral amide group.

(51) Treatment of dihydro-TCNAQs with Pd/C in CH_2Cl_2 caused its dehydrogenation to the corresponding TCNAQs. Therefore, the catalytic oxidation of **2** to **4** by dibromo-TCNAQ **1h** under CT excitation conditions could be realized (turnover > 10) when the photoreaction was conducted in the presence of Pd/C (ref 41). A similar protocol could make it possible in the future to conduct the kinetic resolution of *rac*-**2** using a catalytic amount of chiral TCNAQs.

ing from the corresponding anthraquinones **5b**−**f**. Analytical and spectral data are given in Supporting Information.

Preparation of Racemic Diol *rac*-2. This material was obtained in 62% yield from acenaphthenequinone and 4-methoxyphenyllithium by modifying the reported procedure.[52]

Preparation of Anthraquinones 5a−d and 5f. To a solution of (*R*)-(+)-1-phenylethylamine (2.62 g, 21.7 mmol) in 50 mL of dry $CHCl_3$ was added anthraquinone-2-carbonyl chloride (6.45 g, 23.8 mmol). After the mixture was refluxed for 3 h, the solvent was removed under reduced pressure. The residue was recrystallized from CH_3CN to give 2-[(*R*)-1-phenylethylcarbamoyl]-9,10-anthraquinone **5a** (6.69 g) as yellow needles in 87% yield. Other quinones, **5b**−**d** and **5f**, were similarly prepared by starting from the corresponding chiral amines with an (*R*)-configuration. Most of the amines are commercially available, and (*R*)-1-phenylisobutylamine was prepared as described in the literature.[27] Analytical and spectral data are given in Supporting Information.

Preparation of Anthraquinone 5e. To a solution of secondary amide **5a** (500 mg, 1.41 mmol) in dry THF (15 mL) was added NaH (60% in oil, 113 mg, 2.83 mmol) at 50 °C. After gas evolution ceased, CH_3I (2.7 mL, 43.4 mmol) was added to the red solution at 40 °C, and the mixture was stirred for 15 h at this temperature. The mixture was diluted with water and extracted with $CHCl_3$. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration and removal of the solvent, the residue was chromatographed on SiO_2 to give 2-[methyl-(*R*)-1-phenylethylcarbamoyl]-9,10-anthraquinone **5e** (516 mg) as a yellow solid in 99% yield. Analytical and spectral data are given in Supporting Information.

Determination of Association Constants (K_{CT}). In the presence of a large excess of pinacol **2**, K_{CT} values of the EDA complexes of **1a** were determined in CH_3CN and $CHCl_3$ by a spectrophotometric procedure based on the Benesi−Hildebrand relationship[46] at 23 °C. In all cases, linear correlations were observed, indicating a 1:1 molar ratio for the EDA complex. In these measurements, the concentration of **1a** is 2 × 10^{-3} mol dm^{-3} and those of **2** are 0.10−0.15 mol dm^{-3}. Errors are 5% (*rac*-**2**−**1a**), 15% [(*R,R*)-**2**−**1a**] and 20% [(*S,S*)-**2**−**1a**], respectively, for the values obtained in MeCN. Those for the values measured in $CHCl_3$ are 10%. Molar extinction coefficients for [(*R,R*)-**2**−**1a**] and [(*S,S*)-**2**−**1a**] are 200 and 400 at 440 nm in MeCN, respectively. The CT absorption bands for the diastereomeric EDA complexes are given in the Supporting Information.

CT Excitation Reactions of EDA Complexes. The typical procedures are as follows. An NMR tube containing a degassed solution of **1a** (2.0 × 10^{-2} mol dm^{-3}) and *rac*-**2** (2.0 × 10^{-2} mol dm^{-3}) in 0.6 mL of CD_3CN was immersed in a cold bath (0 °C) and irradiated by a 500-W Xe lamp through a Corning 3-72 glass cutoff filter (λ > 435 nm). The progress of the reaction was monitored by ^{1}H NMR spectroscopy. After 1 h, the mixture was separated by SiO_2 preparative TLC (MeOH:$CHCl_3$ = 1:30) followed by HPLC (SiO_2; AcOEt/$CHCl_3$ = 1:150) to isolate **1a**, **2**, and 4.[53] The enantiomeric excess of recovered **2** was determined by CHIRALCEL-OD-H (0.46 cm ϕ × 25 cm; EtOH/*n*-hexane = 1:1; flow rate of 0.5 mL min^{-1}). The retention time of (*R,R*)-(−)-**2** is 9.7 min and that of (*S,S*)-(+)-**2** is 13.4 min (separability factor α = 1.38; resolution R_s = 1.64; see Figure S7). Other EDA complexes were similarly irradiated, and the photolyzates were analyzed as described above. The CD spectrum of recovered **2** was also measured when necessary to determine the small ee values precisely. The temperature-dependence of the photoreaction could not be investigated because of the limited solubility of **1** at low temperature. At higher temperatures, subsequent transformation of **3a** into four isomers by thermal 1,5-H shift[43] made the reaction too complicated to analyze.

Redox Potential Measurements. Redox potentials were measured by cyclic voltammetry in dry MeCN containing 0.1 mol dm^{-3} Et_4NClO_4 as a supporting electrolyte. Ferrocene undergoes 1e-oxidation at +0.38 V under the same conditions. All of the values shown in the text are in *E*/V vs SCE.

Acknowledgment. This work was supported by grants from the Ministry of Education, Science and Culture, Japan (nos. 14654139, 15350019). We thank Prof. Tamotsu Inabe (Hokkaido University) for use of the X-ray structure analysis system. MS spectra were measured by Dr. Eri Fukushi and Mr. Kenji Watanabe at the GC-MS & NMR Laboratory (Faculty of Agriculture, Hokkaido University). Elemental analyses were conducted by Ms. Akiko Maeda at the Center for Instrumental Analysis (Hokkaido University).

Supporting Information Available: Physical data of TCNAQs **1** and AQs **5** and details of X-ray analyses. ORTEP drawings (Figures S1−S6) and structural data for the X-ray analyses (positional and thermal parameters, bond distances and angles in CIF format) of **1a**, **1f**, *rac*-**2**·EtOH, (*S,S*)-(+)-**2**·EtOH, and (*S,S,S,S*)-**7**; and the HPLC chart of (+)-**2** (Figure S7). CT absorption bands of [(*S,S*)-(+)-**2**−**1a**] and [(*R,R*)-(−)-**2**−**1a**] (Figure S8). Procedure of optical resolution of pinacol **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0505324

(52) (a) Bachmann, W. E.; Chu, E. J. *J. Am. Chem. Soc.* **1936**, *58*, 1118. (b) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (2H, d, *J* = 8.3 Hz), 7.64 (2H, dd, *J* = 6.9, 8.3 Hz), 7.37 (2H, d, *J* = 6.9 Hz), 7.17 (4H, AA′XX′), 6.88 (4H, AA′XX′), 3.82 (6H, s), 2.15 (2H, s).

(53) (a) Letsinger, R. L.; Lansbury, P. T. *J. Am. Chem. Soc.* **1956**, *78*, 2648. (b) ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (2H, dd, *J* = 7.2, 2.1 Hz), 7.80 (4H, AA′XX′), 7.58−7.49 (4H, m), 6.85 (4H, AA′XX′), 3.84 (6H, s).