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Molecular Recognition by Chalcogen Bond: Selective Charge-transfer Crystal Formation of Dimethylnaphthalene with Selenadiazolotetracyanonaphthoquinodimethane

Yusuke Ishigaki,^[a] Kota Asai,^[a] Henri-Pierre Jacquot de Rouville,^[b] Takuya Shimajiri,^[a] Valérie Heitz,^[b] Hiroshi Fujii-Shinomiya,^[c,d] and Takanori Suzuki*^[a]

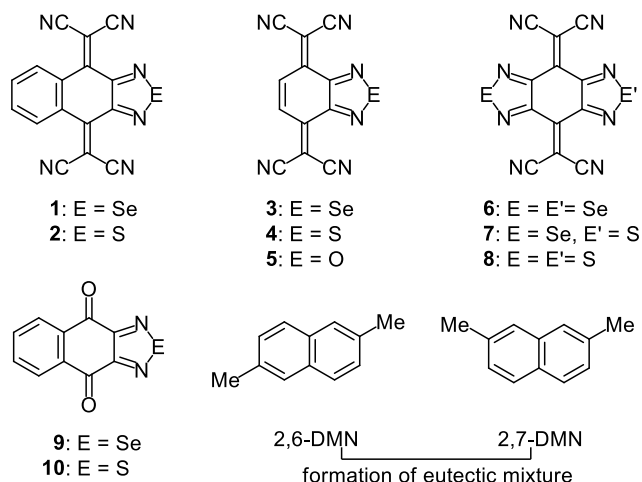
In memory of François Diederich and Tsutomu Miyashi

Abstract: The title nonplanar electron acceptor (**1**) fused with a selenadiazole ring selectively forms a crystalline charge-transfer complex (CT crystal) with 2,6-dimethylnaphthalene (2,6-DMN). On the other hand, the sulfur analogue (**2**) has less recognition ability and forms CT crystals with both 2,6- and 2,7-DMN. X-ray analyses of **1**, **2**, and their CT crystals revealed that the Se ••• N chalcogen bond (ChB) in **1** is strong enough to determine the crystal packing with the formation of a cavity suitable for 2,6-DMN. On the contrary, ChB through S ••• N contact in **2** competes with other weak interactions such as a C-H ••• N hydrogen bond. The stronger ChB involving Se is the key for **1** to separate 2,6-DMN (>97 wt%) from a complex isomer mixture containing ca. 10 wt% each of 2,6- and 2,7-DMN by a simple, efficient and straightforward mixing-filtration-heating process.

Introduction

Directional short contacts are of primary importance in stabilizing supramolecular systems. Indeed, hydrogen bonds are the most prevalent stabilizing interaction in biological architectures due to their directionality and relative strength in comparison to other weak interactions. However, protein structures can also be stabilized by directional short contacts between a divalent sulfur and an oxygen atom.^[1] More generally, these short contacts have been conceptualized as the interaction between an electrophilic chalcogen atom (E) and electron donor atoms (D) acting as a Lewis base.^[2] This stabilizing interaction (R-E ••• D, where R is an electron-withdrawing group) was reported in the solid state in the late 1960's^[3] but has gained a renewed interest over the last decade. Nowadays, it is referred to as the chalcogen bond (ChB).^[4] The directionality of the ChB was explained by the existence of at least one σ -hole on the E atom, which defines a positive electrostatic potential region in the direction opposite of the R-E bond.^[5] Thus, the E atom acts as a Lewis acid that can be bound by a Lewis base through

Formula



$n(D) \rightarrow \sigma^*(E-R)$ electron donation. Interestingly, E atoms can present two σ -holes, thus allowing the interaction of two donor atoms simultaneously. The stability of the ChB is influenced by the nature of the E atom (Te > Se > S >> O), the nature of the electron-deficient R-group, the R-E ••• D angle (close to linear) and the Lewis basicity of D.^[6] A better understanding of these factors has led to application of the ChB in several fields of chemistry, such as supramolecular chemistry^[7] and catalysis.^[8] Even if the ChB is usually characterized by looking at the sum of the van der Waals (vdW) radii in the solid state, this highly directional interaction has scarcely been used in crystal engineering of organic compounds.^[9]

Crystal engineering takes advantage of intermolecular interactions in the context of crystal packing to rationalize the design of new solids with desired physical and chemical properties.^[10] The crystal is described as the predictable assembly of molecules into networks of desired geometries, i.e., a supermolecule.^[11] Consequently, the molecular arrangement in the crystal relies on the nature of the interacting functional groups, also called supramolecular synthons, between molecules in the crystal. These supramolecular synthons allow a retrosynthetic approach by the straightforward determination of node connectivity in the crystals. Two major features of supramolecular synthons can be identified: i) their chemical nature and ii) their relative geometry. Therefore, the use of ChB synthons in crystal engineering is promising due to their high directionality. The [E ••• NC] motif is a supramolecular synthon of choice since it is chemically robust.^[12] We previously used this supramolecular synthon in tetracyanoquinodimethane (TCNQ)-type compounds fused with 1,2,5-chalcogenadiazole(s) (**3** – **8**, Formula).^[13] Interestingly, the linearly-extended molecular networks formed by bis(thiadiazolo)-TCNQ (**8**) in the

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solid state created two-dimensional cavities^[14] allowing the separation of (pseudo)centrosymmetric *p*-disubstituted benzenes from their isomer mixtures by a simple mixing-filtration-heating process (Scheme 1).

This report describes the preparation of two new tetracyanonaphthoquinodimethane (TCNNQ) derivatives fused with a chalcogenadiazole ring (**1** and **2**) and their redox properties.^[15] In addition, the selective formation of CT crystals between **1** and 2,6-dimethylnaphthalene (2,6-DMN) towards its 2,7-isomer is demonstrated. Finally, this selective CT crystal formation was used to separate 2,6-DMN from a complex isomer mixture in catalytic reforming petroleum oil.

Results and Discussion

Molecular design

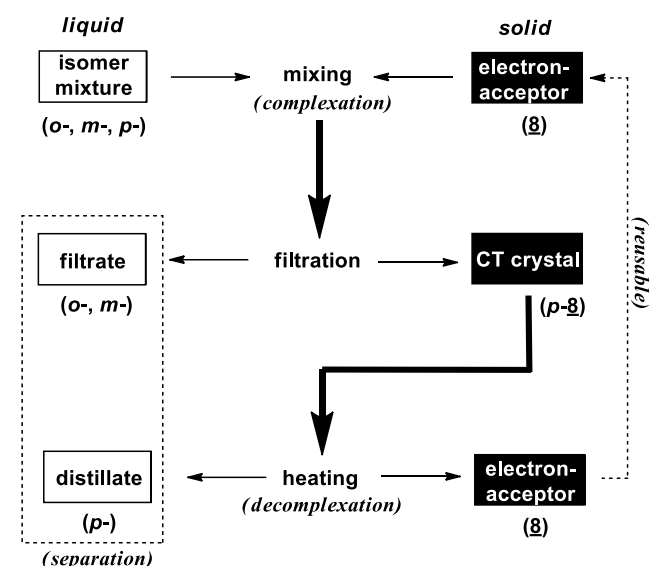
In both derivatives **1** and **2**, C≡N ••• E-N short-contacts were envisioned to drive molecular packing based on favorable geometric and electronic parameters. Indeed, the organization of these supramolecular synthons in the node structure are expected to lead to decreased steric hindrance in the solid state compared to the well-known chalcogenadiazole square-dimer motif^[16] (Scheme 2a,b). In addition, resonance structures reveal an enhanced electron-deficient character of the E atom and an increased electron-donating character of the N atom of the cyano groups in these compounds, which stabilizes the overall assembly (Scheme 2c).

Furthermore, both derivatives **1** and **2** have a curved π -system and were designed to create three-dimensional cavities in the solid state. These cavities are expected to form CT crystals selectively with fused aromatics such as functionalized naphthalene compounds.

Preparation and redox properties of **1** and **2**

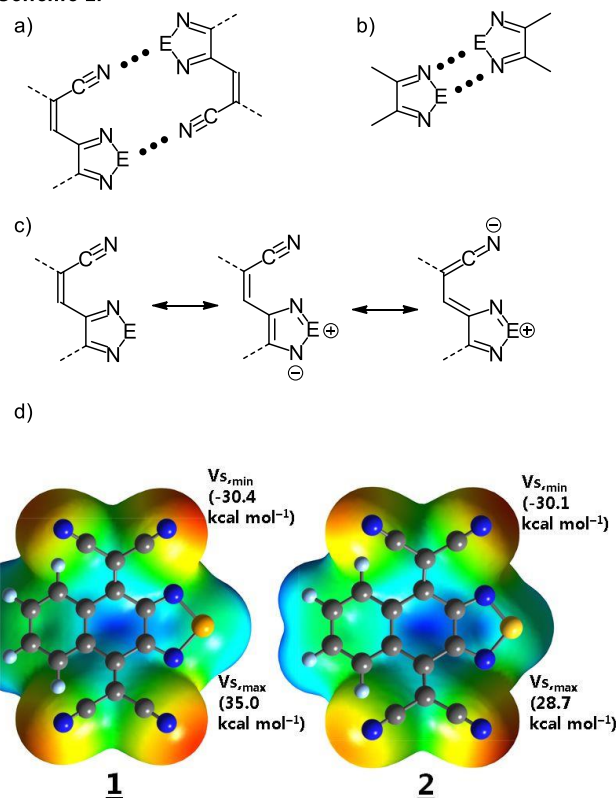
From the corresponding naphthoquinone derivatives^[17] fused with a chalcogenadiazole ring (**9** and **10**, Formula), yellow crystals of **1** and **2** were obtained upon condensation reactions with malononitrile in the presence of TiCl₄^[18] in respective yields of 74% and 89%. According to DFT calculations for **1** and **2** [M06-2X/6-31G(d,p)], contribution of the polarization form (Scheme 2c) is indicated as shown by the electrostatic potentials (Scheme 2d, Figure S1). Thus, more negative $V_{s,min}$ (−30.4 and −30.1 kcal mol^{−1}, respectively) is predicted for cyano N atom in **1** and **2** than in TCNNQ (−27.5 kcal mol^{−1}) without a fused heterocycle. Furthermore, the more positive $V_{s,max}$ values on the chalcogen atoms in **1** and **2** (35.0 and 28.7 kcal mol^{−1}, respectively) are calculated than in the case of the parent selenadiazole (19.3 kcal mol^{−1}) and thiadiazole (13.6 kcal mol^{−1}), respectively. From the more positive $V_{s,max}$, stronger ChB is expected in **1** than in **2**, which is consistent with previous reports comparing the ChB in selenadiazole and thiadiazole derivatives.^[16a]

Scheme 1.



Scheme 1. Simple mixing-filtration-heating process for separation of a certain isomer from the mixture as exemplified by separation of *p*-disubstituted benzenes from the corresponding isomer mixtures by electron acceptor **8**.

Scheme 2.



Scheme 2. (a) Connection of two chalcogenadiazolo-TCNQ molecules by ChB through C≡N ••• E-N contacts. (b) Connection of two chalcogenadiazoles by ChB through 2N-2E square-dimer-type contacts. (c) Polarization of cyanovinylchalcogenadiazole substructure. (d) Electrostatic potentials in **1** and **2** calculated by DFT method [M06-2X/6-31G(d,p)] (isoval = 0.0004).

According to voltammetric analyses in CH₃CN (Figure S2), these compounds undergo reversible two-stage one-electron reduction to give the corresponding dianions. The more negative potentials for **1** (E_1 -0.35 V, E_2 -0.46 V vs SCE in CH₃CN) than for **2** (-0.22, -0.41 V) indicates that **1** is a slightly weaker electron acceptor with a higher LUMO. For Wurster-type^[19] electron acceptors (e.g., TCNQ), aromatization of the central ring is one of the driving forces for facile one-electron reduction. The more negative E_1 for **1** than for **2** can be explained by the less aromatic nature of naphthoselenadiazole than the S-congener, as in the case of the weaker aromaticity of selenophene than of thiophene. When the naphthochalcogenadiazole unit accepts an electron, the less aromatic Se-congener would be reduced more easily. In fact, NLUMO of **1** or **2** has coefficients mainly on this heterocycle (Figure S1), and E_3 for **1** (-1.38 V) is less negative than that for **2** (-1.54 V).

The small separation between E_1 and E_2 in **1** and **2** than in **3** (+0.04, -0.43 V) and **4** (+0.12, -0.38 V) without a fused benzene ring can be explained by the nonplanar structures^[20] of **1** and **2**. Thus, upon two-electron transfer, a change in geometry^[21] from a folded neutral form to a twisted dianionic form (Scheme 3a) is expected, as in other benzo-fused quinodimethane derivatives. The DFT calculation also predicted a curved π -skeleton for **1** and **2** (Scheme 3b), which is characterized by the dihedral angles summarized in Table 1. The steric repulsion between the *peri*-hydrogens and cyano groups is mainly relieved by folding of the central hexagon (α : 25.6° for **1** and 24.7° for **2**, respectively), and the twisting of exocyclic double bonds (β : 27.6° for **1** and 26.9° for **2**, respectively) is discernable due to the different steric demands of benzene and chalcogenadiazole, which are fused to each side of the TCNQ skeleton.

Complexation of **1** and **2** with 2,6- and 2,7-DMN

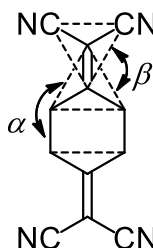
Upon admixing a yellow solution of **1** and a colorless solution of 2,6-DMN in CH₂Cl₂ followed by slow evaporation, CT crystal of 2,6-DMN•**1** (1:2) was obtained as red plates. Comparisons of the IR spectra ($\nu_{\text{C=N}}$: 2227 cm⁻¹ for **1** and 2225 cm⁻¹ for 2,6-DMN•**1**, respectively) indicates that only slight charge transfer (CT) occurs from 2,6-DMN (E^{ox} +1.46 V vs SCE in CH₃CN) to **1**. Attempts to generate CT crystal of **1** with 2,7-DMN (E^{ox} +1.52 V) were unfruitful, and only a mixture of uncomplexed **1** and 2,7-DMN was recovered, since both compounds crystallized out separately. Thus, **1** exhibits high recognition properties toward 2,6-DMN over its 2,7-isomer. Similar behavior was observed when CH₃CN or benzene was used as a solvent. In hexane, ether, or EtOH, no CT crystals were formed at all.

For the S-congener, 2,6-DMN•**2** (1:2) (red plates) was obtained in a similar manner. It should be noted that 2,7-DMN•**2** (1:1) was generated in the presence of a large excess amount of 2,7-DMN. After evaporation of the solvent, efflorescent red plates could be picked up as single-crystalline specimens from the

polycrystalline solid of 2,7-DMN. Thus, thiadiazolo-TCNNQ **2** was proven to form CT crystals with both 2,6- and 2,7-DMNs.

To confirm that **1** and **2** show different complexation behavior during crystallization but not in solution, the association constants (K_{CT}) were determined for the four electron-donor

Table 1. Dihedral angles^a showing the nonplanarity of **1** and **2**

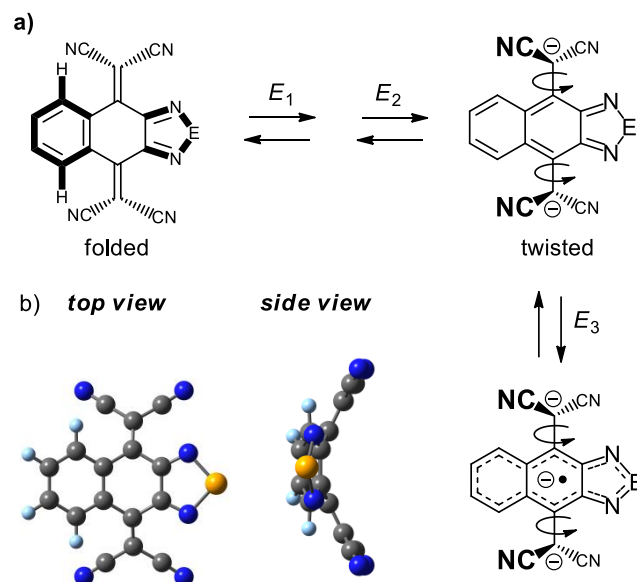
| | α / ° | β / ° | |
|---|--------------|-------------|---|
| <i>Selenadiazolo-TCNNQ</i> | | | |
| calcd. 1 ^b | 25.6 | 27.6 |  |
| uncomplexed 1 | 31.3 | 36.1 | |
| 2,6-DMN• 1 (1:2) | 29.2 | 32.8 | |
| <i>Thiadiazolo-TCNNQ</i> | | | |
| calcd. 2 ^b | 24.7 | 26.9 | |
| uncomplexed 2 -tri ^c | 27.5 | 32.3 | |
| uncomplexed 2 -mono ^d | 23.3 | 25.6 | |
| 2,6-DMN• 2 (1:2) | 28.6 | 32.6 | |
| 2,7-DMN• 2 (1:1) | 20.5 | 24.5 | |

^aValues are averaged over the assumed C_s symmetry. The esd for the experimental values is less than 0.2° unless otherwise noted.

^bGeometries were optimized by DFT method [M06-2X/6-31G(d,p)].

^ctriclinic form with two independent molecules and larger esd values of 0.6°. ^dmonoclinic form.

Scheme 3.



Scheme 3. a) Redox scheme for **1** and **2**. The first two electron reduction processes (E_1 and E_2) are accompanied by geometrical change whereas the third reduction process (E_3) corresponds to the electron capture at the tricyclic heterocycle. b) Folded structure of **1** calculated by DFT method [M06-2X/6-31G(d,p)].

acceptor (EDA) complexes in CH_2Cl_2 at 0 °C. The CT absorption band appears as an extended absorption tail around 500-650 nm, which corresponds to the red color of the solutions (Figure S3). According to the Benesi-Hildebrand equation, a linear correlation was observed in all cases by assuming a 1:1 ratio. The K_{CT} values are 0.55 and 0.50 $\text{mol}^{-1} \text{dm}^3$ for 2,6-DMN - **1** and 2,7-DMN - **1**, respectively. The values for 2,6-DMN - **2** and 2,7-DMN - **2** (0.41 and 0.52 $\text{mol}^{-1} \text{dm}^3$, respectively) are very similar to the EDA complexes of **1**. At any event, no significant recognition was observed in solution for 2,6- and 2,7-DMN by **1** and **2**.

Crystal structures of **1** and its CT crystal

X-ray structural analysis (Table S1) of the light yellow crystal of uncomplexed selenadiazolo-TCNNQ **1** revealed that it had a butterfly-shaped geometry (Figure S4). Selected dihedral angles (Table 1) indicate that **1** has a curved π -plane in crystal, as predicted by the DFT calculation for an isolated gaseous molecule. The packing arrangement of uncomplexed **1** is mainly characterized by two kinds of ChB through $\text{C}\equiv\text{N} \cdots \text{Se}-\text{N}$ contacts [(i) and (ii)]. The geometries of ChB can be described by the distance (D) of $\text{C}\equiv\text{N} \cdots \text{E}$ as well as two angles (θ_1 : $\angle \text{C}\equiv\text{N} \cdots \text{E}$; θ_2 : $\angle \text{N} \cdots \text{E}-\text{N}$) (Table 2). A linear array of three atoms of $\text{N} \cdots \text{E}-\text{N}$ ($\theta_2 \sim 180$) can warrant large stabilization of ChB by considering the σ -hole around the chalcogen atom. On the other hand, $\text{C}\equiv\text{N} \cdots \text{E}$ can be either linear ($\theta_1 \sim 180$) or perpendicular ($\theta_1 \sim 90$) depending on the participation of the sp_2 lone pair or 2p orbital of the cyano group, respectively.

By the ChB through contact (i), two molecules of **1** form a centrosymmetric dyad as shown in Scheme 2a. A similar dyad was also observed in selenadiazolo-TCNQ **3**^[13c] without a fused benzene ring, and a similar association pattern is seen in the networks of bis(chalcogenadiazole) derivatives **6** - **8**.^[14b] The dyad is further connected by ChB through contact (ii) along the crystallographic b axis, thus forming an infinite "dyad-ribbon" network (Figure 1). The D values of (i) and (ii) are both much smaller than the sum of vdW radii of $\text{N} \cdots \text{Se}$ (3.50 Å);^[22] by 10% and 13%, respectively (Table 2a). Thus, as also supported by suitable contact angles (θ_1 and θ_2), the ChB is proven to be a strong and important director of the crystal packing of **1**. The dyad-ribbon networks are further connected to each other along the c axis by weak hydrogen bonds through a $\text{C}-\text{H} \cdots \text{N}\equiv\text{C}$ contact (iii) (Table 2b), and thus a two-dimensional sheet-like structure is formed on the bc plane. Since the sheets are repeated along the a axis without significant interaction, the most characteristic feature is the sheet-like structure composed of dyad-ribbon networks.

Quite similar dyad-ribbon networks are formed by ChB through the $\text{C}\equiv\text{N} \cdots \text{Se}-\text{N}$ contacts [(i) and (ii)] in 2,6-DMN•**1** (1:2) CT crystal (Table S1), showing that ChB in **1** is strong enough to be maintained upon complexation. When the $\text{C}-\text{H} \cdots \text{N}\equiv\text{C}$ hydrogen bonds are broken, however, the original sheet-like structure is separated. Between the two dyad-ribbons, an inclusion cavity for 2,6-DMN is generated (Figure 2). Close

inspection indicated that three molecules of each dyad-ribbon participate to compose the cavity, which are connected by $\text{C}-\text{H} \cdots \text{N}\equiv\text{C}$ bonds [(iii)] at different sites from those in uncomplexed **1**. Along with the two additional molecules, the dicyanomethylene group of which is located nearly in the same plane as the molecular plane of 2,6-DMN, a three-dimensional cavity is composed of 8 molecules of **1** (Figure 3).

Table 2. Geometrical description^a for (a) ChB and (b) $\text{C}-\text{H} \cdots \text{N}\equiv\text{C}$ hydrogen bond^b in **1** and **2**

a)

b)

| (a) | | $D / \text{Å}$ | $\theta_1 / ^\circ$ | $\theta_2 / ^\circ$ |
|--|-------|----------------|---------------------|---------------------|
| <i>Selenadiazolo-TCNNQ</i> | | | | |
| uncomplexed 1 | (i) | 3.16 | 115 | 156 |
| uncomplexed 1 | (ii) | 3.04 | 159 | 177 |
| 2,6-DMN• 1 (1:2) | (i) | 3.27 | 121 | 154 |
| 2,6-DMN• 1 (1:2) | (ii) | 2.99 | 160 | 168 |
| <i>Thiadiazolo-TCNNQ</i> | | | | |
| uncomplexed tri- 2 ^c | (i) | 3.21 | 118 | 170 |
| uncomplexed tri- 2 ^c | (ii) | 3.17 | 124 | 156 |
| uncomplexed-mono- 2 ^d (none) | | | | |
| 2,6-DMN• 2 (1:2) | (i) | 3.38 | 121 | 151 |
| 2,6-DMN• 2 (1:2) | (ii) | 3.08 | 162 | 166 |
| 2,7-DMN• 2 (1:1) | (i) | 3.34 | 97 | 139 |
| (b) | | $d / \text{Å}$ | $\phi_1 / ^\circ$ | $\phi_2 / ^\circ$ |
| <i>Selenadiazolo-TCNNQ</i> | | | | |
| uncomplexed 1 | (iii) | 2.73 | 129 | 127 |
| 2,6-DMN• 1 (1:2) | (iii) | 2.72 | 146 | 128 |
| <i>Thiadiazolo-TCNNQ</i> | | | | |
| uncomplexed tri- 2 ^c | (iii) | 2.69 | 140 | 137 |
| uncomplexed tri- 2 ^c | (iv) | 2.67 | 114 | 150 |
| uncomplexed tri- 2 ^c | (v) | 2.67 | 117 | 148 |
| uncomplexed tri- 2 ^c | (vi) | 2.57 | 147 | 172 |
| uncomplexed tri- 2 ^c | (vii) | 2.57 | 155 | 168 |
| uncomplexed mono- 2 ^d (i) | | 2.70 | 117 | 127 |
| uncomplexed mono- 2 ^d (ii) | | 2.53 | 142 | 135 |
| 2,6-DMN• 2 (1:2) | (iii) | 2.70 | 146 | 129 |
| 2,7-DMN• 2 (1:1) | (ii) | 2.80 | 141 | 125 |
| 2,7-DMN• 2 (1:1) | (iii) | 2.69 | 157 | 158 |
| 2,7-DMN• 2 (1:1) | (iv) | 2.60 | 154 | 128 |

^aThe esd for the distances is less than 0.1 Å. The esd for the angles is less than 1°. ^bAll of the C-H groups are those at the fused benzene ring of **1** and **2**. ^ctriclinic form with two independent molecules, ^dmonoclinic form.

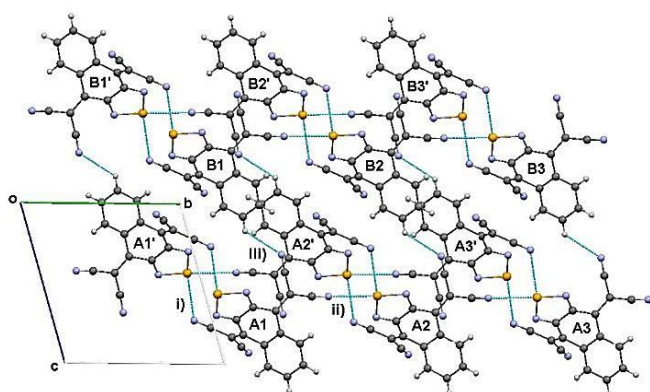


Figure 1. Sheet-like structure composed of dyad-ribbon networks in uncomplexed **1**. Molecules A1 and A1' forms dyad by ChB through contact (i). Molecules A1, A2, and A3 (as well as A1', A2', and A3') are connected by ChB through contact (ii) to form the dyad-ribbon network. Two dyad-ribbons (A1-A3' and B1-B3') are connected by C-H...N≡C bonds (iii) at A1 and B1.

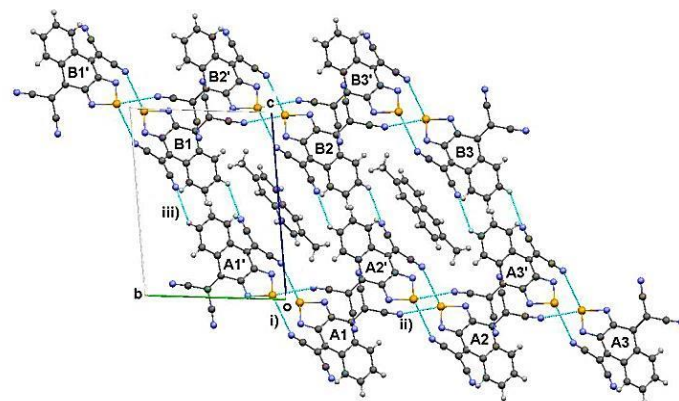


Figure 2. Cavity formation between two dyad-ribbon networks in 2,6-DMN•**1** (1:2) CT crystal. Molecules A1 and A1' forms dyad by ChB through contact (i). Molecules A1, A2, and A3 (as well as A1', A2', and A3') are connected by ChB through contact (ii) to form the dyad-ribbon network. Two dyad-ribbons (A1-A3' and B1-B3') are connected by C-H...N≡C bonds (iii) at different sites (A1' and B1) from those of uncomplexed **1**.

In the cavity, 2,6-DMN is stacked with the dicyanomethylene moiety of two molecules of **1**. The shortest C...C contact in the π - π overlap is 3.30 Å, which is less than the sum of the vdW radii (3.40 Å)^[22] and indicates the presence of CT interaction. The recognition of 2,6-DMN over 2,7-DMN by this cavity is due to the two molecules of **1** in which the dicyanomethylene group is nearly coplanar to 2,6-DMN, thus exhibiting several short atomic contacts in the lateral direction (Figure S5), indicating that misplacement of 2,7-DMN in this cavity causes severe steric repulsion. This is why the three-dimensional cavity of **1** selectively accommodates 2,6-DMN, which is the outstanding difference from the clathrate compounds of **8** that exhibit limited selectivity for 2,6-DMN.^[14b] Unlike **1** with a curved π -system, planar **8** forms a two-dimensional cavity (Figure S10), showing that a three-dimensional cavity is more appropriate for discriminating between 2,6- and 2,7-DMNs, which have a similar molecular shape to form a eutectic mixture.^[23]

Crystal structures of **2** (polymorphs) and its CT crystals

The 2,6-DMN•**2** (1:2) (Table S1, Figure S6) is isomorphous to the Se-congener, 2,6-DMN•**1** (1:2). The inclusion cavity for 2,6-DMN is formed by ChB through C≡N...S-N contacts [(i) and (ii)] as well as a C-H...N≡C bond [(iii)] (Table 2). While the geometrical values of (iii) are quite similar to those in 2,6-DMN•**1**, the ChB seems much weaker than that in the Se-congener. Thus, the *D* value of (i) is nearly the same as the sum of vdW radii of N...S (3.35 Å)^[22] while that of (ii) is smaller by 8%. In this way, the relative importance of C-H...N≡C is increased as a decisive factor for directing the crystal packing of **2** compared to **1**.

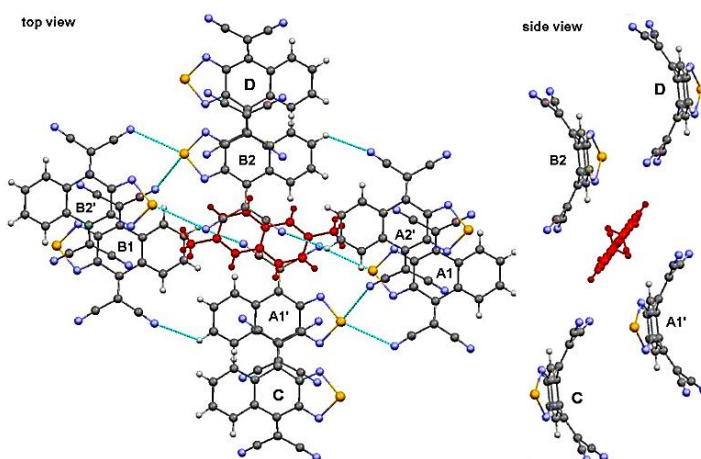


Figure 3. Inclusion of 2,6-DMN in the cavity in 2,6-DMN•**1** (1:2) CT crystal. Molecules A1, A1', and A2' are part of a dyad-ribbon whereas B1, B2, and B2' belong to another dyad-ribbon. Molecules of A1' and B1 as well as A2' and B2 are connected by C-H...N≡C bonds. 2,6-DMN was sandwiched by A1' and B2 through π - π overlaps (shortest C...C contact of 3.30 Å). There are several contacts (2.93, 2.94, and 3.04 Å) between the C-H groups of 2,6-DMN and cyano nitrogen of molecules C and D, the dicyanomethylene group of which is located nearly in the same plane to the molecular plane of 2,6-DMN, and thus the cavity cannot accommodate 2,7-DMN.

In fact, when we analyzed the structures of two polymorphs of uncomplexed **2** (**2**-tri: triclinic, $P\bar{1}$, $Z = 4$; **2**-mono: monoclinic $P21/c$, $Z = 4$), the crystal structures are mainly characterized by the networks formed by multiple C-H \cdots N \equiv C bonds. For **2**-tri (Table S1, Figure S7), there are two crystallographically independent molecules (mol-1 and mol-2) in the crystal. ChB through C \equiv N \cdots S-N contacts [(i) and (ii)] are present, however, a much larger number of C-H \cdots N \equiv C bonds [(iii) - (vii)] are also noted (Table 2). No dyad was formed in the crystal. These intermolecular interactions [two ChB, (i) and (ii); five C-H \cdots N \equiv C, (iii) - (vii)] are found only between mol-1 and mol-2. Thus, each mol-1 is connected to seven different mol-2 whereas each mol-2 is connected to seven different mol-1 (Figure S7). The resulting three-dimensional network in **2**-tri is apparently governed by C-H \cdots N \equiv C bonds that overwhelm the number of ChB.

In another polymorph of **2** (**2**-mono) (Table S1), there is no ChB in the crystal. Instead, two kinds of C-H \cdots N \equiv C contacts [(i) and (ii)] (Table 2b) connect the molecules to form a "dyad-ribbon" network (Figure S8). The absence of ChB is common to thiadiazolo-TCNQ **4**^[13c] without a fused benzene ring, which forms a dyad by C-H \cdots N \equiv C bonds as does oxadiazolo-TCNQ **5**. All of the above crystallographic results regarding **2** indicate that the ChB in **2** is much weaker than that in the Se-congener **1**, and the C-H \cdots N \equiv C bond can play an important role in determining the crystal structure of **2** and its CT crystals. Since there are four C-H groups in **2** in contrast to only one chalcogen atom, a large variety of molecular networks would be formed based on C-H \cdots N \equiv C bonds. Thus, it could be possible that **2** forms CT crystals with other DMNs (e.g., 2,7-DMN), in which crystal packing is mainly controlled by C-H \cdots N \equiv C bonds.

In the crystal packing of 2,7-DMN•**2** (1:1) (Table S1), we found one contact for ChB [(i)] and three contacts for C-H \cdots N \equiv C bonds [(ii) - (iv)]. The geometrical features (large D , small θ_2) of the former (Table 2a) indicate that ChB is less effective. The dyad of **2** is generated by C-H \cdots N \equiv C bonds [(ii)]. The dyad is further connected by another C-H \cdots N \equiv C bond [(iv)] along the crystallographic b axis, to form an infinite dyad-ribbon network. Another C-H \cdots N \equiv C bond [(iii)] as well as ChB through contact (i) connect the dyad-ribbons to form a sheet-like structure in the [201] plane (Figure 4a). Each molecule of **2** in the sheet is involved in forming an A-D-A-D mixed stack (Figure 4b), in which two independent molecular overlaps (Figure S9) are repeated along the crystallographic c axis. Thus, above or below the sheet-like structure of **2**, a layer is formed that contains only 2,7-DMN. Although the molecules of **2** are connected by CH \cdots N \equiv C bonds, this CT crystal is not considered to be a clathrate compound, since no cavity is formed for 2,7-DMN.

Selenadiazolo-TCNNQ **1** renders the nearly perfect separation of 2,6-DMN from the isomer mixture, whereas thiadiazolo-TCNNQ **2** does not. This quite different behavior can be rationalized in terms of the strength of ChB (Se \cdots N vs S \cdots N), which plays an important role in molecular recognition in the solid state.

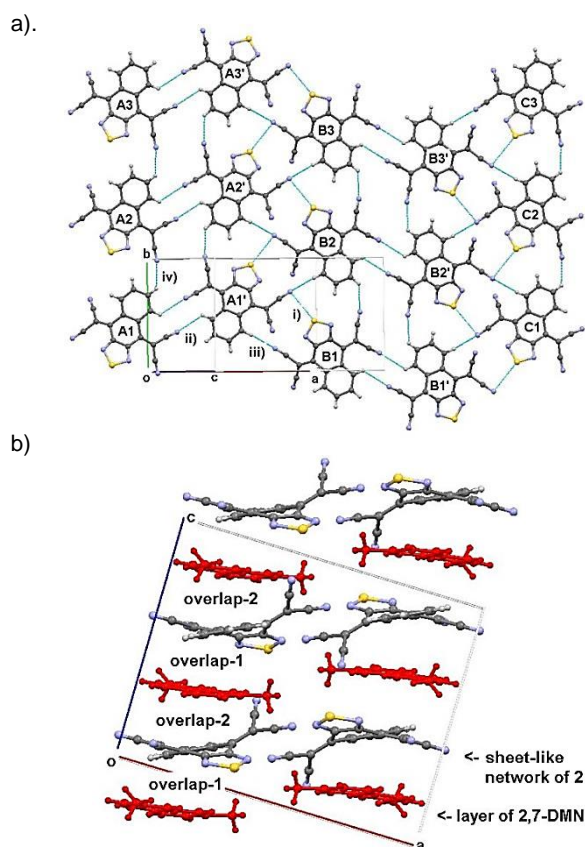


Figure 4. (a) Sheet-like structure composed of dyad-ribbon networks in 2,7-DMN•**2** (1:1). Molecules A1 and A1' forms dyad by C-H \cdots N \equiv C bond [(ii)]. Molecules A1, A2, and A3 (as well as A1', A2', and A3') are connected by C-H \cdots N \equiv C bond [(iv)] to form the dyad-ribbon network. Two dyad-ribbons (A1-A3' and B1-B3') are connected by C-H \cdots N \equiv C bond [(iii)] and weak ChB through contact (i). The molecule C1 has the coordinates of (x+2, y, z+1) relative to A1 (x,y,z). (b) A-D-A-D mixed stack in 2,7-DMN•**2**. Sheet-like structures of **2** and layers of 2,7-DMN are repeated alternately along the c axis.

Separation of 2,6-DMN from a mixture by a mixing-filtration-heating process

Finally, to demonstrate the utility of the outstanding recognition properties of **1**, selective CT crystal formation of 2,6-DMN•**1** (1:2) was conducted by using a mixture obtained as a fraction at bp 250-270 °C from catalytic reforming petroleum oil. This C₁₂ liquid contains 9.7 wt% 2,6-DMN and 9.4 wt% 2,7-DMN, respectively. It also contains other DMNs and several aromatic compounds (Table S2), and thus is suitable for examining the high selectivity toward 2,6-DMN.

After **1** (83 mg) was mixed with the C₁₂ liquid (1.23 g), the resulting suspension was filtered to give CT crystals (84 mg), which were heated at 145 °C (14 mmHg) to give 12 mg of

colorless distillate accompanied by the recovery of **1** (72 mg). GC analysis of the resulting distillate showed that it is 97.2 wt% 2,6-DMN, with slight contamination by 2,7-DMN (1.1 wt%) and other compounds. This observation shows the high selectivity in the crystallization process between **1** and 2,6-DMN in comparison to other isomers of DMN. This outcome reflects the efficient self-sorting^[24] process between **1** and 2,6-DMN resulting from their electronic and geometrical complementarity in the solid state. As a control experiment, a similar mixing-filtration-heating process was conducted using the S-congener **2**. The resulting distillate contained not only 2,6-DMN (37.8 wt%) but also 2,7-DMN (10.5 wt%) as well as other DMN isomers (39.8 wt%). This study clearly demonstrates that the observed self-sorting process is under thermodynamic control. Indeed, the stronger ChB between molecules of **1** than between molecules of **2** undoubtedly governs the high selectivity for 2,6-DMN in this self-sorting process. This result shows the potential of crystal engineering for the purification of a polyaromatic guest from complex mixtures. Especially, purification of 2,6-DMN^[25] from raw material is an interesting approach for industrial applications since this molecule is a precursor of polyethylenenaphthalate, a promising engineering plastic.^[26]

Conclusions

In this work, we have shown that a cyanovinyl-substituted chalcogenadiazole moiety is an important subunit for ChB through C≡N ••• E-N contacts. Electron-accepting selenadiazolo-TCNNQ **1** with a curved π -system can form a dyad-ribbon network by ChB in its uncomplexed crystal, and the same motif is also found in the CT crystal with 2,6-DMN. In the latter, a three-dimensional cavity is formed between two dyad-ribbons, which can only accommodate 2,6-DMN and is not suitable for its regioisomers. Thus, **1** can form CT crystals only when the donor guest can be incorporated in the cavity formed by the "preorganized" dyad-ribbon network. Otherwise, **1** and the unsuitable donor crystallize out separately, as in the combination of **1** and 2,7-DMN. This is the reason why **1** can separate 2,6-DMN from the isomer mixture via a simple mixing-filtration-heating process.

On the other hand, ChB through C≡N ••• S-N contacts in thiadiazolo-TCNNQ **2** is weaker, and thus cannot always be the determining factor for crystal packing. Actually, one of the polymorphs of uncomplexed **2** (**2**-tri, triclinic form) has a crystal structure with two ChB, but the molecules are further connected through five C-H ••• N≡C bonds. In another polymorph (**2**-mono, monoclinic form), no ChB is present and crystal packing is characterized by C-H ••• N≡C bonds. Although 2,6-DMN•**2** (1:2) is crystallized isomorphously to the Se-congener [2,6-DMN•**1** (1:2)] to select 2,6-DMN among other isomers, **2** can form other packing arrangements by C-H ••• N≡C bonds so that **2** forms CT complexes with other isomers as in the case of 2,7-DMN•**2** (1:1). Accordingly, the ability of **2** to recognize DMN

isomers is low due to the "induced fit"-type complexation via C-H •••N≡C bonds.

For the future design of clathrate-host molecules for molecular recognition, a "preorganized" supramolecular synthon formed by ChB would make a good molecular design concept, and the use of Se (or Te) would be more promising by strengthening network formation without being perturbed by other interactions such as C-H ••• X bonds or halogen bonds.^[27] While the additional use of other weak interactions would lead to more sophisticated recognition, care should be taken so that some other interaction never overwhelms ChB.

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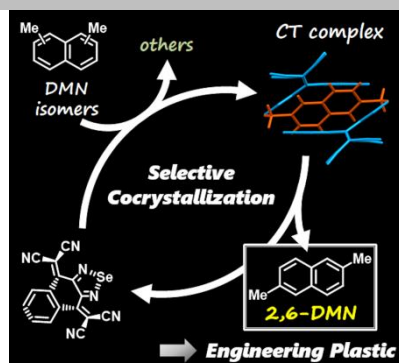
Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

Chalcogen makes the change:

Highly selective cocrystallization with 2,6-dimethylnaphthalene (2,6-DMN) allows the title selenadiazole-based electron acceptor to separate 2,6-DMN from the isomer mixture by an effective Se ••• N chalcogen bond whereas the sulfur congener shows only low selectivity due to the competing C-H ••• N hydrogen bond, which overwhelms the S ••• N bond.



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Molecular Recognition by Chalcogen Bond: Selective Charge-transfer Crystal Formation of Dimethylnaphthalene with Selenadiazolotetracyanonaphthoquinodimethane