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# Dicyanovinyl Heterotetracenes: Synthesis, Solid-State Structures, and Photophysical Properties

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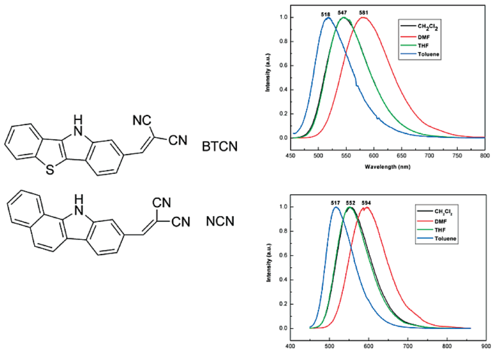

Two asymmetrically substituted dicyanovinyl heterotetracenes are synthesized and characterized. Single-crystal X-ray diffractions indicate both intermolecular hydrogen bonds and $\pi$-stacking existing in the solid-state structures. The solvatochromic behaviors of the two heterotetracenes were investigated in a variety of solvents. Both experimental and computational results suggest that the two heterotetracenes have low-lying lowest unoccupied molecular orbitals and thus may be potential n-type or bipolar organic semiconductors for organic electronics.

## Introduction

Linearly fused acenes and heteroacenes occupy a prominent position of research in $\pi$-conjugated organic small molecules because of their attractive electronic and optical properties.[1] In particular, many heteropentacenes have been reported owing to the benchmark of pentacene[2] for thin film organic field-effect transistors (OFETs). Among these heteroacenes, sulfur[3] or/and nitrogen[4,5] atoms are introduced widely to tune the solid-state structure and electronic structure of the organic semiconductors and meanwhile overcome the shortcomings of acenes such as low solubility and instability. We found that the reported molecules mainly introduced sulfur or nitrogen as the bridging atom, and most of them behave as p-type organic semiconductors.[6,7]

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[1] Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028–5048.

[2] (a) Lin, Y.; Gundlach, D.; Nelson, S.; Jackson, T. *IEEE Trans. Electron Devices* **1997**, *44*, 1325. (b) Kelley, T.; Muyres, D.; Baude, P.; Smith, T.; Jones, T. *Mater. Res. Symp. Proc.* **2003**, *771*, L6.5.1.

[3] (a) Du, C.; Guo, Y.; Liu, Y.; Qiu, W.; Zhang, H.; Gao, X.; Liu, Y.; Qi, T.; Lu, K.; Yu, G. *Chem. Mater.* **2008**, *20*, 4188–4190. (b) Tang, M. L.; Okamoto, T.; Bao, Z. *J. Am. Chem. Soc.* **2006**, *128*, 16002–16003. (c) Ebata, H.; Miyazaki, E.; Yamamoto, T.; Takimiya, K. *Org. Lett.* **2007**, *9*, 4499–4502. (d) Laquindanum, J. G.; Katz, H. E.; Lovinger, A. J. *J. Am. Chem. Soc.* **1998**, *120*, 664–672. (e) Gao, J.; Li, R.; Li, L.; Meng, Q.; Jiang, H.; Li, H.; Hu, W. *Adv. Mater.* **2007**, *19*, 3008–3011. (f) Wex, B.; Kaafarani, B. R.; Schroeder, R.; Majewski, L. A.; Burckel, P.; Grell, M.; Neckers, D. C. *J. Mater. Chem.* **2006**, *16*, 1121–1124.

[4] (a) Miao, Q.; Nguyen, T.-Q.; Someya, T.; Blancher, G. B.; Nuckolls, C. *J. Am. Chem. Soc.* **2003**, *125*, 10284–10287. (b) Ma, Y.; Sun, Y.; Liu, Y.; Gao, J.; Chen, S.; Sun, X.; Qiu, W.; Yu, G.; Cui, G.; Hu, W.; Zhu, D. *J. Mater. Chem.* **2005**, *15*, 4894–4898. (c) Wu, Y.; Li, Y.; Garder, S.; Ong, B. S. *J. Am. Chem. Soc.* **2005**, *127*, 614–618. (d) Li, Y.; Wu, Y.; Garder, S.; Ong, B. S. *Adv. Mater.* **2005**, *17*, 849–853. (e) Miao, S.; Bangcuyo, C. G.; Smith, M. D.; Bunz, U. H. F. *Angew. Chem., Int. Ed.* **2006**, *45*, 661–665.

[5] Qi, T.; Guo, Y.; Liu, Y.; Xi, H.; Zhang, H.; Gao, X.; Liu, Y.; Lu, K.; Du, C.; Yu, G.; Zhu, D. *Chem. Commun.* **2008**, 6227–6229.

[6] (a) Briseno, A.; Miao, Q.; Ling, M.-M.; Reese, C.; Meng, H.; Bao, Z.; Wudl, F. *J. Am. Chem. Soc.* **2006**, *128*, 15576–15577. (b) Mishra, A.; Ma, C.-Q.; Bauerle, P. *Chem. Rev.* **2009**, *109*, 1141–1276. (c) Payne, M. M.; Parkin, S. R.; Anthony, J. E.; Kuo, C.-C.; Jackson, T. N. *J. Am. Chem. Soc.* **2005**, *127*, 4986–4987. (d) Yamamoto, T.; Takimiya, K. *J. Am. Chem. Soc.* **2007**, *129*, 2224–2225. (e) Sirringhaus, H.; Friend, R. H.; Wang, C.; Leuninger, J.; Mullen, K. *J. Mater. Chem.* **1999**, *9*, 2095–2101.

[7] (a) Tian, H.; Shi, J.; Yan, D.; Wang, L.; Geng, Y.; Wang, F. *Adv. Mater.* **2006**, *18*, 2149–2152. (b) Miyata, Y.; Terayama, M.; Minari, T.; Nishinaga, T.; Nemoto, T.; Isoda, S.; Komatsu, K. *Chem. Asian J.* **2007**, *2*, 1492–1504.

DOI: 10.1021/jo901381f

However, n-type or bipolar materials[8] needed for complementary circuits present a challenge for chemists. On one side, it is difficult to find a suitable electrode for the injection of electrons into the lowest unoccupied molecular orbital (LUMO) levels of the n-type semiconductors because the LUMO levels ( > 3.0 eV)[9] of most n-type semiconductors are incompatible with the work function of gold (4.8−5.1 eV). Low work function electrodes such as Ca, Mg, and Al are not environmentally stable.[8a] On the other side, the susceptibility of organic semiconductors to water and oxygen[10] under ambient conditions makes them technologically unattractive. One strategy to overcome the problems is to increase the electron affinity of a semiconducting material, which could not only lower the LUMO levels but also improve its sensitivity to oxygen and water. It has been reported that adding strong electron-withdrawing groups such as fluorine, cyano, or diimide moieties to a semiconducting core could lower the electron affinity.[8a] As we know, acenes[11] and heteroacenes[12] with strong electron-withdrawing substituents are scarcely studied.

As an analogue of pentacene, tetracene[13] and its heterocycle derivatives received less attention due to their limited $\pi$ systems. For the reported heterotetracenes, Takimiya and co-workers introduced two sulfur and selenium atoms in the backbone of tetracene and obtained a series of derivatives of heterotetracene and also constructed high-performance OFET devices.[14] Bao's group[3b] and Tao's group[15] reported anthra[2,3-*b*]thiophene, an analogy of tetracene, and its device application simultaneously. Bunz's group reported the synthesis, solid-state structures, and aromaticity studies of two dialkynylated diazatetracenes and their parent diazatetracenes.[16] To the best of our knowledge, the introduction of sulfur or/and nitrogen and also an electron-withdrawing group together in the tetracene-like system has not been reported. Functionalization of tetracene with electron-withdrawing groups is intriguing for the development of stable n-type or bipolar semiconducting materials because these functionalized acenes may possess lower LUMO levels than their correlative parent acenes. This strategy can also help to create molecular materials with low energy electronic transitions based on donor−acceptor interactions.[17]

Dicyanomethylene- and tricyanovinyl-substituted[18] oligothiophenes with high electron mobilities have been reported. However, dicyanovinyl-substituted oligomers[19] usually introduce bulky substituent spacers such as triarylamine, and dicyanovinyl-substituted acenes and heteroacenes have not been considered. Here, we selected the dicyanovinyl group as the substituent and heterotetracene with sulfur or/and nitrogen as core because of the following advantages: (a) The long, platelike molecular shape of heterotetracene can retain the conjugation of the whole $\pi$-system and thus facilitate carrier transport. (b) The heteroatom affects not only on the electronic structures but also on the solid-state structures led to easy control of the highest occupied molecular orbital (HOMO)−LUMO energy gap and an increase the air stability of the materials. (c) The cyano groups have strong electron-accepting properties and may be useful for lower electron affinity.

In this paper, we report the synthesis, solid-state structures, and photophysical properties of novel indolo[3,2-*b*]benzo[*b*]thiophene or indolo[3,2-*b*]naphthalene-based heteroacenes asymmetrically end-capped with a dicyanovinyl group, i.e., BTCN and NCN. To the best of our knowledge, this is the first report of tetracene-like compounds with an electron-withdrawing group. The target compounds are characterized in detail. Their electronic properties are studied by using UV−vis/fluorescence spectroscopy, cyclic voltammetry, and density functional theory (DFT). The solid-state structures of BTCN and NCN have been investigated, and the solvatochromic behaviors of the two compounds in different solvents were studied.

## Results and Discussion

The synthesis of the target compounds BTCN and NCN is outlined in Scheme 1. Suzuki coupling reaction between 4-bromo-3-nitrobenzaldehyde and benzo[b]thiophene-2-boronic acid or naphthalene-2-boronic acid gave compound **3a** or **3b**, respectively, in good yields (70−71%). Cyclization of compound **3a** or **3b** with an improved Cadogan reaction[5,20]

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(8) (a) Zaumseil, J.; Sirringhaus, H. *Chem. Rev.* **2007**, *107*, 1296–1323. (b) Wurthner, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 1037–1039. (c) Newman, C. R.; Frisbie, C. D.; Filho, D. A. S.; Bredas, J. L.; Ewbank, P. C.; Mann, K. R. *Chem. Mater.* **2004**, *16*, 4436–4451.

(9) (a) Hutchison, G. R.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **2005**, *127*, 16866–16881. (b) Jones, B. A.; Facchetti, A.; Wasielewski, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 15259–15278.

(10) (a) Yoon, M.-H.; Dibenedetto, S.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2005**, *127*, 1348–1349. (b) Wang, Z.; Kim, C.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 13362–13363.

(11) (a) Sakamoto, Y.; Suzuki, T.; Kobayashi, M.; Gao, Y.; Fukai, Y.; Inoue, Y.; Sato, F.; Tokito, S. *J. Am. Chem. Soc.* **2004**, *126*, 8138–8140. (b) Inoue, Y.; Sakamoto, Y.; Suzuki, T.; Kobayashi, M.; Gao, Y.; Tokito, S. *Jpn. J. Appl. Phys.* **2005**, *44*, 3663–3668. (c) Sakamoto, Y.; Suzuki, T.; Kobayashi, M.; Gao, Y.; Inoue, Y.; Tokito, S. *Mol. Cryst. Liq. Cryst.* **2006**, *444*, 225–232. (d) Ong, B. S.; Keoshkerian, B. *J. Org. Chem.* **1984**, *49*, 5002–5003.

(12) (a) Geramita, K.; Mcbee, J.; Tilley, T. D. *J. Org. Chem.* **2009**, *74*, 820–829. (b) Cho, D. M.; Parkin, S. R.; Watson, M. D. *Org. Lett.* **2005**, *7*, 1067–1068. (c) Wang, Y.; Parkin, S. R.; Gierschner, J.; Watson, M. D. *Org. Lett.* **2008**, *10*, 3307–3310.

(13) (a) Gaudlach, D. J.; Nichols, J. A.; Zhou, L.; Jackson, T. N. *Appl. Phys. Lett.* **2002**, *80*, 2925–2927. (b) Cicoira, F.; Santato, C.; Dinelli, F.; Murgia, M.; Loi, M. A.; Biscarini, F.; Zamboni, R.; Heremans, P.; Muccini, M. *Adv. Funct. Mater.* **2005**, *15*, 375–380. (c) Abthagir, P. S.; Ha, Y.-G.; You, E.-A.; Jeong, S.-H.; Seo, H.-S.; Choi, J.-H. *J. Phys. Chem. B* **2005**, *109*, 23918–23924. (d) Chen, Z.; Mller, P.; Swager, T. M. *Org. Lett.* **2006**, *8*, 273–276. (e) Reichwagen, J.; Hopf, H.; Guerzo, A. D.; Belin, C.; Bouas-Laurent, H.; Desvergne, J.-P. *Org. Lett.* **2005**, *7*, 971–974.

(14) (a) Takimiya, K.; Kunugi, Y.; Konda, Y.; Ebata, H.; Toyoshima, Y.; Otsubo, T. *J. Am. Chem. Soc.* **2006**, *128*, 3044–3050. (b) Takimiya, K.; Ebata, H.; Sakamoto, K.; Izawa, T.; Otsubo, T.; Kunugi, Y. *J. Am. Chem. Soc.* **2006**, *128*, 12604–12605. (c) Izawa, T.; Miyazaki, E.; Takimiya, K. *Adv. Mater.* **2008**, *20*, 3388–3392.

(15) Valiyev, F.; Hu, W. S.; Chen, H. Y.; Kuo, M. Y.; Chao, I.; Tao, Y. T. *Chem. Mater.* **2007**, *19*, 3018–3026.

(16) Miao, S.; Brombosz, S. M.; Schleyer, P. R.; Wu, J. I.; Barlow, S.; Marder, S. R.; Hardcastle, K. I.; Bunz, U. H. *J. Am. Chem. Soc.* **2008**, *130*, 7339–7344.

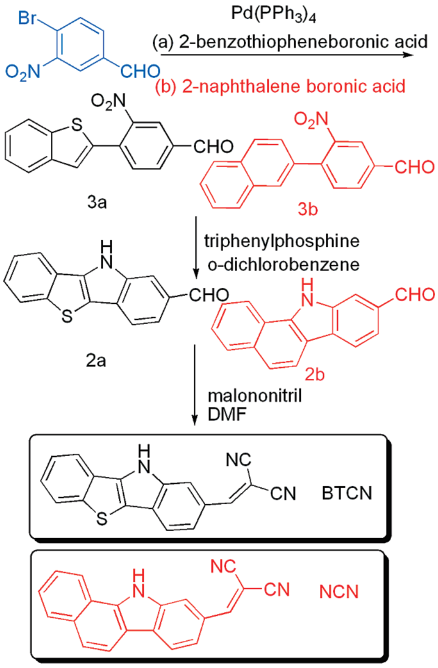
(17) Casado, J.; Delgado, M. C. R.; Merchan, M. C. R.; Hernandez, V.; Navarrete, J. T. L.; Pappenfus, T. M.; Williams, N.; Stegner, W. J.; Johnson, J. C.; Edlund, B. A.; Janzen, D. E.; Mann, K. R.; Orduna, J.; Villacampa, B. *Chem.—Eur. J.* **2006**, *12*, 5458–5470.

(18) (a) Handa, S.; Miyazaki, E.; Takimiya, K.; Kunugi, Y. *J. Am. Chem. Soc.* **2007**, *129*, 11684–11685. (b) Cai, X.; Burand, M. W.; Newman, C. R.; Filho, D. A. S.; Pappenfus, T. M.; Bader, M. M.; Brdas, J.-L.; Mann, K. R.; Frisbie, C. D. *J. Phys. Chem. B* **2006**, *110*, 14590–14597. (c) Pappenfus, T. M.; Chesterfield, R. J.; Frisbie, C. D.; Mann, K. R.; Casado, J.; Raff, J. D.; Miller, L. L. *J. Am. Chem. Soc.* **2002**, *124*, 4184–4185. (d) Kunugi, Y.; Takimiya, K.; Toyoshima, Y.; Yamashita, K.; Aso, Y.; Otsubo, T. *J. Mater. Chem.* **2004**, *14*, 1367–1369.

(19) (a) Xia, P. F.; Feng, X. J.; Lu, J.; Tsang, S. W.; Movileanu, R.; Tao, Y.; Wong, M. S. *Adv. Mater.* **2008**, *20*, 4810–4815. (b) Qin, P.; Zhu, H.; Edvinsson, T.; Boschloo, G.; Hagfeldt, A.; Sun, L. *J. Am. Chem. Soc.* **2008**, *130*, 8570–8571. (c) Breitung, E. M.; Shu, C. -F.; MaMahon, R. J. *J. Am. Chem. Soc.* **2000**, *122*, 1154–1160.

(20) (a) Cadogan, J. I. G.; Cameron-Wood, M. *Proc. Chem. Soc.* **1962**, 361. (b) Cadogan, J. I. G.; Cameron-Wood, M.; Mackie, R. K.; Searle, R. J. G. *J. Chem. Soc.* **1965**, 4831–4837. (c) Cadogan, J. I. G. *Synthesis* **1969**, 11–17. (d) Cadogan, J. I. G. *Organophosphorus Reagents in Organic Synthesis*; Academic Press: London, 1979; Chapter 6. (e) Freeman, A. W.; Urvoy, M.; Criswell, M. E. *J. Org. Chem.* **2005**, *70*, 5014–5019.

**SCHEME 1. Synthesis of BTCN and NCN**



using a slight excess of triphenylphosphine in *o*-dichlorobenzene afforded compound **2a** or **2b**. Notably, for compound **3b**, 4-($\beta$-naphthalene)-3-nitrobenzaldehyde, the α-position of naphthalene was more favorable to the cyclization, thus giving bent indolo[3,2-*a*]naphthalene derivative. The final asymmetrically substituted heterotetracene derivatives BTCN and NCN were obtained by condensing the aldehydes **2a** or **2b** with excess malononitrile in DMF in the presence of pyridine. The target compounds BTCN and NCN are soluble in most common organic solvents, so purification of crude products was easily performed by recrystallization. All newly synthesized, asymmetrically substituted heterotetracenes were fully characterized by $^{1}$H NMR, $^{13}$C NMR, elemental analysis, and X-ray single-crystal diffraction and were found to be in good agreement with their structures.

To estimate the position of the frontier orbital of BTCN and NCN, density functional theory (DFT) calculations were performed using Gaussian 03[21] at the B3LYP/6-31G(d) level. For BTCN and NCN, as shown in Figure 1, the largest coefficients in HOMO are mainly located on the heteroacene backbone. As expected, the coefficients in LUMO are mostly located on the dicyanovinyl groups. The calculated results indicate that there may be intramolecular charge transfer, which has been confirmed by the optical spectra discussed in the following section. The energy values of the HOMO and LUMO orbital of BTCN and NCN were also calculated by using DFT (the HOMO values are −5.81, −5.80 eV; the LUMO values are −2.75, −2.74 eV; the band gap values are 3.06, 3.06 eV for BTCN and NCN, respectively). The DFT results show that BTCN and NCN both have low-lying HOMO and LUMO levels which may be helpful for oxidative stability.

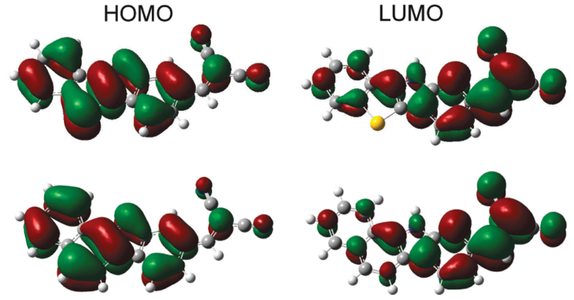


**FIGURE 1.** HOMO and LUMO orbitals of BTCN (top) and NCN (bottom) obtained by DFT calculations.

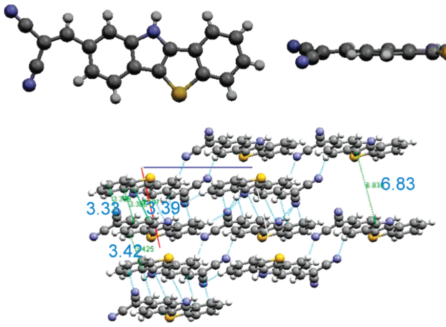


**FIGURE 2.** Solid-state structure of BTCN and a variety of instances between layers viewed down the *b* axis; all values in angstroms.

**Solid-State Structure of Compounds BTCN and NCN.** The solubility of compounds BTCN and NCN is good in common solvents, and they can form crystals easily. We obtained a red plate single crystal of BTCN by slow evaporation of THF solution. An X-ray diffraction was performed on the BTCN single crystal to determine its solid-state structure; see the Supporting Information. As shown in Figure 2, molecules of BTCN are nearly planar with the dicyanovinyl end group deviated only 9.39° from the plane. Interestingly, from the solid-state interactions we can observe that there are two kinds of hydrogen-bond-like short contacts existing in the molecule structure: (a) The imino H atom of pyrrole ring and the N atom of the cyano group of the adjacent molecules are involved with an interatomic distance of 2.276 Å for N−H···N. (b) The other type of C−H···N short contact involves one of the hydrogens of the benzene ring carbon and N atom of the other cyano group, with a slightly longer interatomic distance of 2.649 Å. Head-to-tail dimeric pairs formed in order to optimize the dipole−dipole electrostatic interactions, which alternate induced layer structures. Furthermore, $\pi-\pi$ contacts occurred between an antiparallel pair with three kinds of short distances of 3.339, 3.385, and 3.397 Å, respectively, while distances between the pairs are 3.42 Å and distances between the head molecules of two pairs are 6.83 Å.

Crystals of compound NCN suitable for single-crystal X-ray diffraction studies were grown from cold dichloromethane and hexane solution (volume ratio, 1:2). As shown in Figure 3, the molecule of NCN adopted a configuration similar to that of BTCN except that the dicyanovinyl end group deviated 12.62° from the backbone plane. However, unlike BTCN, there was only one kind of hydrogen-bond-like existing between two adjacent molecules with an interatomic distance of 2.314 Å for N−H···N. Similarly, head-to-tail dimeric pairs induced layer by a layer stacking structure. Also, short distances of 3.36 and 3.39 Å existed within the antiparallel pairs, while distances between the pairs are

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[21] Frisch, M. J. et al. *Gaussian 03, revision C.02*; Gaussian, Inc.: Wallingford, CT, 2004.

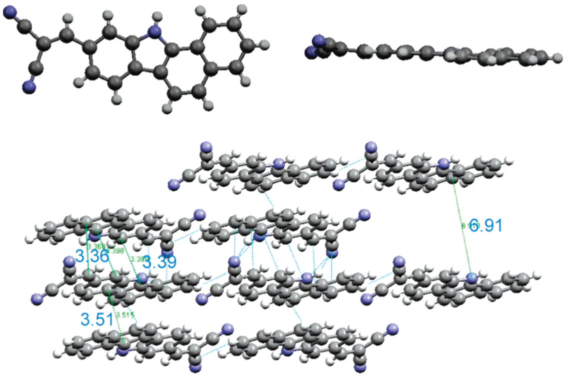

**FIGURE 3.** Solid-state structure of NCN and variety of instances between layers viewed down the *b* axis; all values in angstroms.

3.51 Å and distances between the head molecules of two pairs are 6.91 Å.

These $\pi$-stacking behaviors that occur between BTCN and NCN, induced by dipole−dipole interactions, are interesting for heteroacenes, most of which adopted herringbone packing and are also different from usual $\pi$-stacking arrangements.[22] The double-channel fashion with both hydrogen bonds and C−H$\cdots\pi$ contacts may be helpful for establishment of efficient charge-transport systems.

**Optical Properties.** The photophysical properties of the two heteroacenes were investigated in dilute solutions and in thin films. Figure 4 shows their absorption and fluorescence spectra in $CH_2Cl_2$ solution. The two compounds both show two distinct absorption bands, and absorption peaks were at 385, 445 nm for BTCN and 388, 436 nm for NCN, respectively. The two broad absorption peaks indicated that intramolecular charge transfer occurred in the two D−A molecules, which coincides with the DFT-calculated results. The maximum absorption wavelengths for BTCN and NCN in film exhibited significant red-shift compared to those in solution and located at 527 and 511 nm, respectively, because of the formation of the aggregates. Such a pronounced change of the absorption spectrum is a result of the delocalization of the exciton within the stack layers induced by the $\pi$−$\pi$ interaction.

The maximum emission wavelengths in $CH_2Cl_2$ solutions for BTCN and NCN were 544 and 553 nm, respectively. It is worth noting that the Stokes shift of the fluorescence band of BTCN and NCN in $CH_2Cl_2$ solution was much higher with $\Delta\lambda = 99$ and 117 nm, respectively. The magnitude of the Stokes shift of the two compounds suggested large differences between the excited state reached after absorption and the excited state from which the emission starts.[22] Charge-transfer processes should be fairly effective due to the presence of a $\pi$-donor and a $\pi$-acceptor (dicyanomethylene group).

To gain further insight into the photophysical process within the two compounds, we investigated their absorption and emission behaviors in different solvents. The absorption spectra are nearly independent of solvent polarity in these D−A molecules, indicating a negligible intramolecular interaction between donor and acceptor chromophores in the ground states.[23] However, their emission spectra exhibited very strong solvent dependence. As shown in Figure 5 and Table 1, the maximum emission peak of BTCN changed from 518 nm in toluene to 581 nm in DMF, while for NCN changes occurred from 517 nm in toluene to 594 nm in DMF. These results suggest that the excited states of our molecules possess more polar character than the ground state.

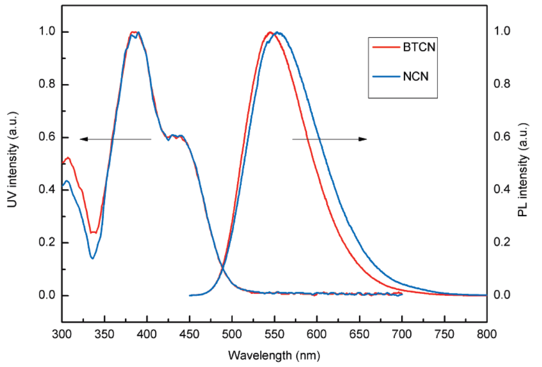

**FIGURE 4.** UV−vis and emission spectra of BTCN and NCN in $CH_2Cl_2$ solution.

**TABLE 1. Optical Properties of BTCN and NCN in Different Solvents**

| | $\lambda_{abs}$[a]/nm | | $\lambda_{lum}$[b]/nm | | | |
|---|---|---|---|---|---|---|
| compd | in $CH_2Cl_2$ | in toluene | in $CH_2Cl_2$ | in THF | in DMF | Stokes shift[c]/nm |
| BTCN | 445 | 518 | 544 | 547 | 581 | 99 |
| NCN | 436 | 517 | 553 | 550 | 594 | 117 |

[a] Measured in a dilute solution ($10^{-5}$ M). [b] Excited at the absorption maxima. [c] Estimated the value in $CH_2Cl_2$.

The effect of acid on the optical properties of the two compounds was also studied (Figure 6 and Supporting Information). Once more, the absorption spectra of BTCN and NCN showed insignificant changes upon addition of HCl, HAc, and TFA (see Supporting Information). However, the emission spectra of the two compounds exhibit red-shifted wavelength maxima along with a successive decrease in the fluorescence intensity upon the addition of acid. Figure 6 (left) showed the change of emission spectrum of BTCN with increasing HAc concentration. Compared with other pyrimidine-containing compounds that can be protonated easily,[24] the nitrogen atoms of the pyrrole unit in our compounds seemed not to be protonated as no significant color change was observed with the addition of acid in the dichloromethane solutions of these compounds. The changes of the emission spectra upon addition of acid may be attributed to solvatochromic behavior as the maximum emission peak of BTCN in pure HAc was located at 577 nm. To confirm the explanation, we measured the emission spectra changes of NCN in $CH_2Cl_2$ with $10^{-2}$ M methanol upon addition of HAc (Figure 6, right). As expected, the emission spectra of NCN exhibit a successive decrease in the fluorescence intensity with the increase of HAc content. But a negligible red-shift of emission spectra was observed because of the presence of strong polarity methanol before

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[22] Curtis, M. D.; Cao, J.; Kampf, J. W. *J. Am. Chem. Soc.* **2004**, *126*, 4318–4328.

[23] Lin, Y.-H.; Wu, H.-H.; Wong, K.-T.; Hsieh, C.-C.; Lin, Y.-C.; Chou, P.-T. *Org. Lett.* **2008**, *10*, 3211–3214.

[24] Achelle, S.; Nouira, I.; Pfaffinger, B.; Ramondenc, Y.; Ple, N.; Rodriguez-Lopez, J. *J. Org. Chem.* **2009**, *74*, 3711–3717.

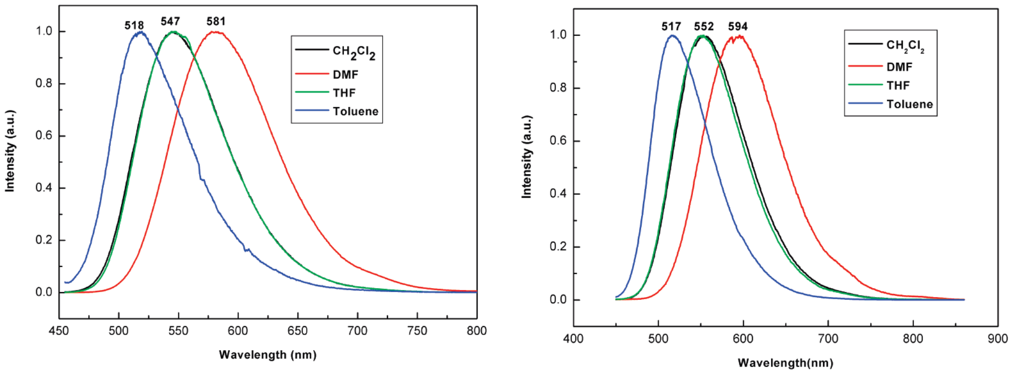

**FIGURE 5.** Emission spectra of BTCN (left) and NCN (right) in different solvents.

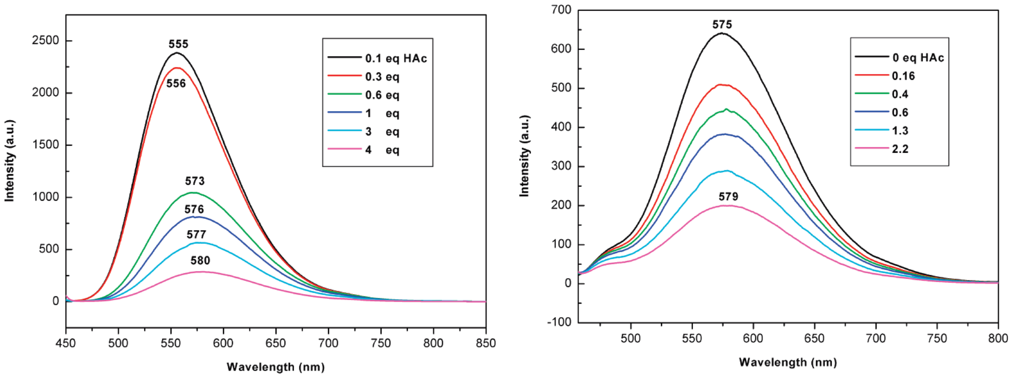

**FIGURE 6.** (Left) Emission spectrum changes of BTCN in $CH_2Cl_2$ with increasing HAc concentration. (Right) Emission spectra changes of NCN in $CH_2Cl_2$ with $10^{-2}$ M methanol upon addition of HAc.

**TABLE 2. Electrochemical Properties and DFT Calculated Results of BTCN and NCN**

| | | | experimental | | | theoretical[e] | | | |
|---|---|---|---|---|---|---|---|---|---|
| compd | $E_{ox}$[a]/V | $E_{red}$[a]/V | HOMO[b]/eV | LUMO[c]/eV | $\Delta E$[d]/eV | HOMO/eV | LUMO/eV | $\Delta E$/eV | $Eg_{opt}$[f]/eV |
| BTCN | 1.29 | −1.42 | −5.46 | −3.69 | 1.77 | −5.81 | −2.75 | 3.06 | 2.12 |
| NCN | 1.34 | −1.33 | −5.42 | −3.72 | 1.70 | −5.80 | −2.74 | 3.06 | 1.97 |
| tetracene[g] | 0.72 | | −5.40 | −3.15 | 2.25 | | | | |

[a] Obtained from the potential at peak of oxidation and reduction. [b] Calculated using the empirical equation: HOMO = $-(4.44 + E_{ox}^{onset})$. [c] Calculated from LUMO = $-(4.44 + E_{red}^{onset})$. [d] Measured using a glassy carbon electrode as a working electrode, a platinum rod as a counter electrode, and Ag/AgCl as a reference electrode in $CH_2Cl_2$ containing 0.1 M $n$-$Bu_4NPF_6$ as a supporting electrolyte at a scan rate of 100 mV/s under an argon atmosphere. [e] Obtained from the DFT results using Gaussian 03 at the B3LYP/6-31G(d) level. [f] Estimated from the onset of absorption spectra of the film of two compounds. [g] Obtained from ref 3b.

addition of HAc. This result further indicated that the acid effect is due to the increase of polarity other than protonation of nitrogen center.

As compared with other tricyanovinyl-substituted hetero-oligomers which have been known to demonstrate intense solvatochromic behavior in absorption spectra,[25] our compounds showed an atypical trend with only observed solvatochromic behavior in the fluorescence spectra. As we know, this is the first report of solvatochromic behavior of dicyanovinyl-substituted heteroacenes.

The redox properties of the two heteroacene derivatives were investigated by cyclic voltammetry (CV, see Table 2). Both BTCN and NCN display quasi-reversible oxidations and reductions under the experimental conditions. The oxidation peak maxima of BTCN and NCN were found at 1.29 and 1.34 V vs $A_g/A_gCl$, respectively. The HOMO levels of compound BTCN and NCN were estimated from the first oxidation onsets to be −5.46 and −5.42 eV, respectively, which coincide with the DFT-calculated results. In the reduction process, BTCN showed lower reduction potential (−1.42 V) with respect to NCN (−1.33 V), indicating that thiophene unit in BTCN shows larger donor property than benzene unit in NCN. Electrochemical band gaps (1.77 and 1.70 eV for BTCN and NCN, respectively) were calculated from the onset potentials of the anodic and cathodic processes and coincide well with the calculated optical band gaps. These redox properties indicate that electron injection is possible and the target compounds would be potential n-type or ambipolar organic semiconductors.

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(25) (a) Pappenfus, T. M.; Burand, M. W.; Janzen, D. E.; Mann, K. R. *Org. Lett.* **2003**, *5*, 1535–1538. (b) Eckert, K.; Schroder, A.; Hartmann, H. *Eur. J. Org. Chem.* **2000**, 1327–1334. (c) Wang, Y.-K.; Shu, C.-F.; Breitung, E. M.; McMahon, R. J. *J. Mater. Chem.* **1999**, *9*, 1449–1452. (d) Garcia, P.; Pernaut, J. M.; Hapiot, P.; Wintgens, V.; Valat, P.; Garnier, F.; Delabouglise, D. *J. Phys. Chem.* **1993**, *97*, 513–516.

In summary, we have synthesized asymmetrical substituted dicyanovinyl heterotetracene compounds. Interesting C−H$\cdots$N interactions were found in the solid structures. Both DFT-calculated results and experimental data indicated that the two electron-deficient heterotetracenes have low-lying LUMOs which may facilitate electron injection. The stable reduction behavior, coupled with their favorable $\pi$-stacking features, makes the heterotetracenes viable candidates for potential n-channel or ambipolar organic semiconductors. Experiments are underway to test this hypothesis.

## Experimental Section

**Synthesis of 8-Dicyanovinyl-6*H*-indolo[3,2-*b*]benzo[*b*]thiophene (BTCN).** At room temperature, malononitrile (0.18 g, 2.73 mmol) was added to a 100 mL two-necked flask containing **2a** (0.67 g, 2.67 mmol) and 50 mL of DMF. After the mixture was stirred for 3 min, pyridine (0.5 mL) was added to the mixture. Then the solution was refluxed for 12 h, after which the resulting mixture was poured into ice−water and red precipitate formed immediately. Crude product BTCN was obtained by filtration as a red solid. Purification of the crude product by recrystallization in acetonitrile afforded a red crystal (0.5 g, 63%). $^1$H NMR (400 MHz, DMSO-*d*, $\delta$): 7.67−7.71 (t, 1H), 7.74−7.77 (t, 2H), 7.47−7.56 (m, 2H), 7.76−7.78 (d, 1H), 7.98−8.00 (d, 1H), 8.09−8.14 (m, 2H), 8.29 (s, 1H), 8.56 (s, 1H), 12.86 (s, 1H). $^{13}$CNMR (100 MHz, DMSO-*d*, $\delta$): 76.72, 114.84, 115.12, 115.62, 116.80, 120.04, 121.68, 122.06, 125.13, 125.43, 126.12, 126.23, 126.62, 140.35, 143.05, 143.99, 162.09. Anal. Calcd for $C_{18}H_9N_3S$: C, 72.22; H, 3.03; N, 14.04. Found: C, 72.15; H, 3.16; N, 13.88.

**Synthesis of 8-Formyl-6*H*-indolo[3,2-*b*]benzo[*b*]thiophene (2a).** Compound **2a** was synthesized with a improved Cadogan cyclization method. A solution of compound **3a** (1.3 g, 4.59 mmol) and $PPh_3$ (3 g, 13.77 mmol) in *o*-DCB (15 mL) was heated to reflux with vigorous stirring. After 12 h, the solvent was stripped under high vacuum, and the resulting dark solid was purified with column chromatography on silica gel with petroleum ether/ethyl acetate (5:1) as the eluent, affording 0.96 g (86%) of **2a** as yellow solid. EI-MS: *m*/*z* 251.3 ($M^+$). $^1$H NMR (400 MHz, DMSO-*d*, $\delta$): 7.39−7.52(m, 2H), 7.76−7.78 (d, 1H), 7.92−7.95 (t, 2H), 8.08 (s, 1H), 8.93 (s, 1H), 10.10 (s, 1H). $^{13}$CNMR (100 MHz, DMSO-*d*, $\delta$): 114.64, 116.22, 119.61, 120.00, 121.44, 125.03, 125.25, 126.03, 126.26, 126.46, 131.65, 140.38, 141.78, 143.49, 192.99. Anal. Calcd for $C_{15}H_9NOS$: C, 71.69; H, 3.61; N, 5.57. Found: C, 71.45; H, 3.47; N, 5.80.

**Synthesis of 4-(Benzo[*b*]thiophene-2-yl)-3-nitrobenzaldehyde (3a).** Into a mixture of benzo[*b*]thiophene-2-boronic acid (2.14 g, 12 mmol) and 4-bromo-3-nitrobenzaldehyde (2.76 g, 12 mmol) in freshly distilled THF (20 mL) was added 2 M $K_2CO_3$ solution (15 mL), and then $Pd(PPh_3)_4$ (100 mg) was added in one portion under argon. The mixture was refluxed for 24 h. The mixture was cooled to room temperature and then extracted with ethyl acetate. The organic layers were dried and evaporated in vacuum. The residue was purified with column chromatography on silica gel with petroleum ether/ethyl acetate (2:1) as the eluent to give pure **3a** (2.41 g, 71%) as an orange yellow solid. EI-MS: *m*/*z* 283 ($M^+$). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.39−7.44 (m, 3H), 7.82−7.87 (m, 3H), 8.11−8.13 (d, 1H), 8.31−8.32 (d, 1H), 10.10 (s, 1H). $^{13}$C NMR (400 MHz, $CDCl_3$) $\delta$ = 122.18, 124.37, 124.47, 124.66, 124.94, 125.03, 125.61, 132.03, 132.63, 133.18, 133.61, 136.19, 136.22, 139.69, 140.59, 189.15. Anal. Calcd for $C_{15}H_9NO_3S$: C, 63.59; H, 3.20; N, 4.94. Found: C, 63.44; H, 3.37; N, 5.30.

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**Supporting Information Available:** Experimental procedures, details, DFT calculation details, solid-state structure analysis, spectra, cyclic voltammetry, and X-ray structure (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.