

Crystal Structure and Phototransistor Behavior of N-Substituted Heptacene

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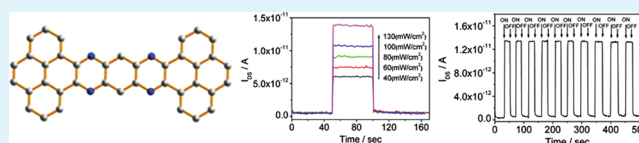
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Supporting Information

ABSTRACT: 6,8,15,17-Tetraaza-1.18,4.5,9.10,13.14-tetrabenzoheptacene (TTH, **1**) has been prepared and characterized by single-crystal X-ray structure analysis. A phototransistor device based on TTH single crystal demonstrated that TTH showed a good performance in signal amplification under the photoconductive effect as well as photocontrolled switches.

KEYWORDS: N-substituted heptacene, single crystal, structure, phototransistor, device fabrication



INTRODUCTION

Recently, N-substituted polycyclic aromatic hydrocarbons (PAHs) have been receiving an increasing research interest because of their potential application in n-type devices.^{1–7} Theoretical calculation results show that this family of molecules not only possesses high electron affinities (3–4 eV), but also has smaller reorganization energies, which might be the benefit in the molecules rearrangement.¹ In addition, the strong intermolecular CH–N interactions in solid state are expected to enhance the electron mobility through tuning the intermolecular stacking and improve the stability of n-channel devices at air conditions.⁸ These predictions strongly encourage us to introduce nitrogen atoms into our previously reported PAH backbones⁹ and study their novel physical properties.

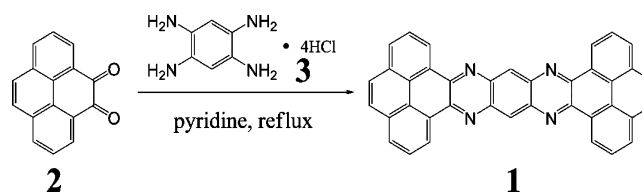
Pyrene-fused heptacenes not only show high stability but also have great performance in light-emitting devices.¹⁰ These interesting factors have led to the successful synthesis of tetraazaheptacene, which is isostructural and isoelectronic to pyrene-fused heptacenes.¹¹ The basic physical studies have already shown that 6,8,15,17-tetraaza-1.18,4.5,9.10,13.14-tetrabenzoheptacene has a red-shift UV–vis spectrum (560 nm) comparing to those (450 nm) of pyrene-fused 6,8,15,17-tetraphenyl-1.18,4.5,9.10,13.14-tetrabenzoheptacene and 1.18,4.5,9.10,13.14-tetrabenzoheptacene (yellow color)^{9d,12} due to the N-atoms replacement. In addition, the investigation by cyclic voltammetry (CV)¹¹ has already indicated that TTH had a smaller bandgap and lower band position. The narrower bandgap and high-electronic affinity together with the unknown spacious arrangement of tetraazaheptacene molecules in solid state initiates us to reinvestigate this material and find its devices' application in phototransistors. Phototransistors are a typical device, which could convert light into either current or

voltage. Phototransistors could have wide applications in compact disk players, sensors, and remote control devices.

RESULTS AND DISCUSSION

TTH (**1**) was synthesized through the condensation reaction between pyrene-dione **2** and the commercially available tetraaminobenzene tetrahydrochloride **3** in a dry pyridine solution at refluxing temperature under N₂ atmosphere according to the previously reported method (Scheme 1).¹¹

Scheme 1. Synthetic Route of Compound 1



The as-prepared product was purified through physical vapor deposition method (the detailed purification process has been provided in the Supporting Information) to give needlelike crystals (Figure 1a). The structure of TTH was determined from single-crystal X-ray diffraction data collected at room temperature on an APEX II CCD diffractometer. Compound TTH adopts a monoclinic unit cell ($a = 24.2945(12)$ Å, $b = 3.8517(2)$ Å, $c = 25.4884(15)$ Å, $\beta = 99.407(3)^\circ$) and space group $P2(1)/n$. Panels b and c in Figure 1 present the crystal

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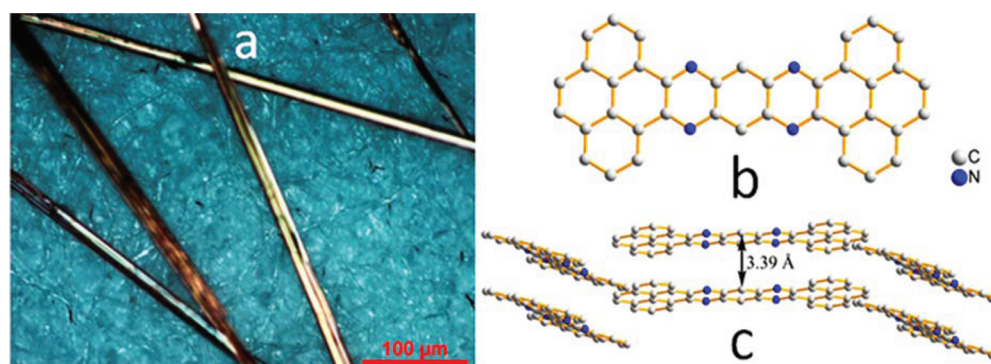


Figure 1. (a) Picture of as-prepared tetraazaheptacene needle crystals. (b) Single-crystal structure of tetraazaheptacene. (c) Molecular stacking of tetraazaheptacene. Carbon and nitrogen atoms are colored in gray and blue, respectively.

structure of TTH in front view and the molecules' stacking in side view, respectively. Different from the isostructural compounds such as 1.18,4.5,9.10,13.14-tetrabenzoheptacene,¹² 6,8,15,17-tetraphenyl-1.18,4.5,9.10,13.14-tetrabenzoheptacene,^{9d} and other twistacene¹³ that have a torsion angle to make the whole molecule out of plane, TTH is flat and all carbon and nitrogen atoms are in one plane. Such geometries might benefit for electrons or holes transport. TTH molecules adopt the face-to-face stacking along the *c* axis. The distance between adjacent molecules is 3.39 Å, which is shorter than van der Waals forces, indicating that there is strong $\pi\cdots\pi$ interactions between intermolecules. Interestingly, there are two types of N \cdots H–C bonds in the structure (see Figure S1 in the Supporting Information): intramolecular and intermolecular bonds. The intramolecular N \cdots H–C bonds, which are shown red dash line (see Figure S1 in the Supporting Information), fall in the ranges of 2.49–2.55 Å. Meanwhile, the intermolecular N \cdots H–C bonds, which are shown green dash line, vary from 2.97 to 3.71 Å. It is clearly shown that the intramolecular N \cdots H–C bond energy is stronger than the intermolecular N \cdots H–C bond energy. The thermal gravimetric analysis measured under nitrogen atmosphere shows that the onset of weight loss begins at 450 °C, which suggests that TTH has a high stability (see Figure S2 in the Supporting Information). The high stability, low bandgap (~ 2.30 eV),¹¹ and strong $\pi\cdots\pi$ interactions together with N \cdots H–C bonds make TTH a promising candidate for phototransistors.

Phototransistors which could be utilized to amplify signals and detect light are sensitive to light and can convert light into electrical signals.^{14–17} Currently, organic phototransistors attract a lot of attention because of their low cost, flexibility, and light weight.^{18–20} Thus, a phototransistor device based on a single crystal of TTH was fabricated. Needlelike single crystal was first transferred onto a cleaned glass substrate, which was obtained after sonicating with pure water, isopropanol, and acetone, each time for 10 min. Figure 2 presents the schematic illustration of the as-fabricated phototransistor device. Silver paste was used as the two electrodes and the light source was a normal xenon lamp.

According to photogenerated charge carriers, a phototransistor can be operated in two modes: a photoconductive mode and a photovoltaic mode.^{13,14,19} In photoconductive mode, the gate voltage (V_G) is zero or smaller than the threshold voltage and the device only can be activated mainly under light illumination. If the gate voltage is larger than the threshold voltage, the device itself is in on-state and light can amplify the drain-source current (I_{DS}). In this situation, the

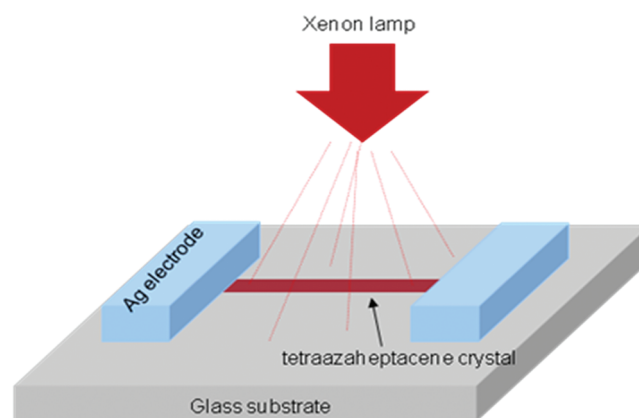


Figure 2. Schematic representation of the typical organic phototransistor fabricated by tetraazaheptacene single crystal.

device is in photovoltaic mode. In our research, the device is thus in photoconductive mode because no gate voltage was applied.¹⁹

Figure 3a shows the current (I_{DS}) as a function of voltages under different light intensities. Phototransistors have a nonzero collector current known as dark current when the device is in absolute darkness, thus a pulsating light is more easily detected since a changing collector current can be differentiated from a static background. The current will increase with the increasing of light intensity and the charge carriers will be generated when the photon energy of light is equal to or higher than the band gap energy of the TTH single crystal. It is clearly observed that the I_{DS} is linearly with light intensity in range of 40–130 mW/cm² without any gate voltage as shown as in Figure 3b. These experimental results suggest that the TTH single-crystal-based organic phototransistor works under the photoconductive effect.

Figure 3c exhibits the dependence of I_{DS} at specific drain-source voltage on light intensity. When the light intensity increases, the current will rise accordingly. Note that the output current increases sharply when the light is applied. During the testing time, the current was stable. The concentration of charge carriers increases as the enhancement of light power. Figure 3d shows the dynamic photoresponse behavior of TTH crystals, which clearly indicates that the TTH-crystal-based device can act as a switch and the ON/OFF ratio is about 1×10^2 . Furthermore, stability test was performed under voltage of 30 V and light intensity of 40 mW/cm², the results are shown in Figure 3e. The device can keep stable under the illumination

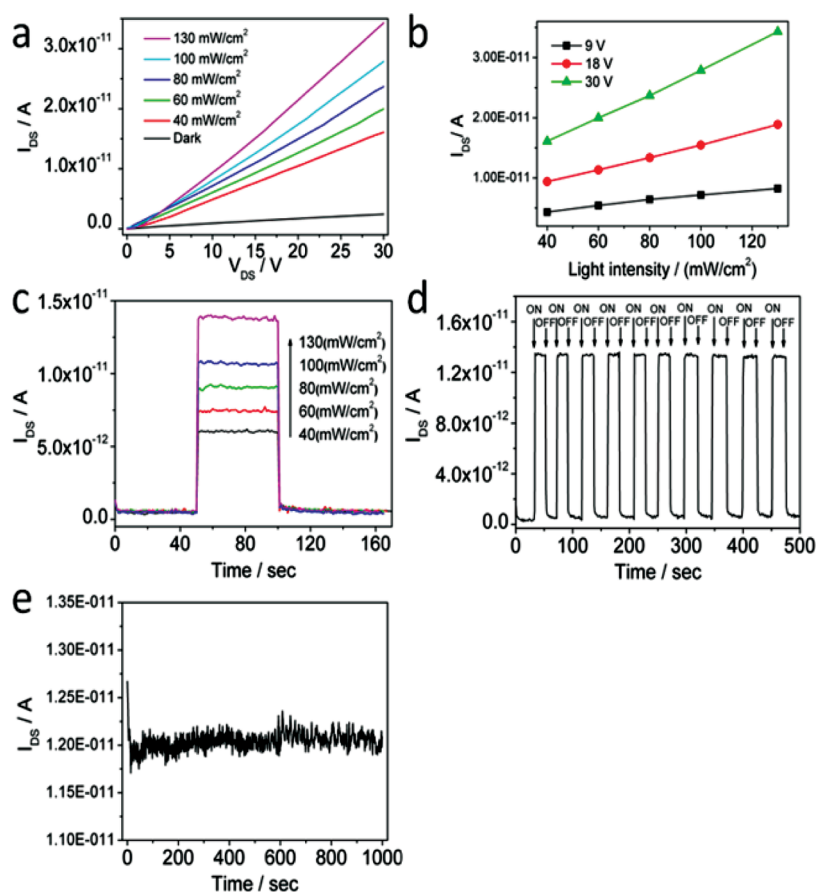


Figure 3. (a) Plot of current (I_{DS}) vs. voltages under different light intensities. (b) Dependence of I_{DS} on light intensity at specific voltages. (c) Dependence of I_{DS} on different input light intensities. (d) Time dependence of dynamic photoresponse behavior of TTH crystals upon the irradiation of 40 mW/cm^2 white light. (e) Stability of TTH single crystal based phototransistors.

of more than 15 min. All results suggest that TTH single crystal can be used as active elements in phototransistors for photodetection or photocontrolled switch.

In conclusion, we have successfully synthesized 6,8,15,17-Tetraaza-1.18,4.5,9.10,13.14-tetrabenzoheptacene, which structure has been characterized by single-crystal X-ray diffraction analysis. The strong π - π interaction together with high electron affinities caused by N-atoms encourages us to investigate its devices' application. In this report, we have already fabricated TTH-single-crystal-based phototransistors and found that these transistors displayed very good performance in signal amplification under the photoconductive effect. In addition, these devices can be functionalized as a photocontrolled switch. Note that all performances on TTH single-crystal-based phototransistors are reversible and reproducible. We do believe that these properties should be able to find some applications in industry. The other devices' applications based on TTH crystals are under investigation.

■ ASSOCIATED CONTENT

Supporting Information

Thermal gravimetric analysis (TGA), FT-IR spectrum, MALDI-TOF spectrum, and crystal data of TTH; purification and crystal growth of TTH; and device fabrication of phototransistor. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Michael, W.; Houk, K. N. *J. Am. Chem. Soc.* **2007**, *129*, 1805–1815.
- (2) (a) Tonzola, C. J.; Alam, M. M.; Kaminsky, W.; Jenekhe, S. A. *J. Am. Chem. Soc.* **2003**, *125*, 13548–13558. (b) Tadokoro, M.; Yasuzuka, S.; Nakamura, M.; Shinoda, T.; Tatenuma, T.; Mitsumi, M.; Qzawa, Y.; Toriumi, K.; Yoshino, H.; Shiomi, D.; Sato, K.; Takui, T.; Mori, T.; Murata, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 5144–5147.
- (3) (a) Hutchison, K. A.; Srdanov, G.; Hicks, R.; Yu, H.; Wudl, F.; Strassner, T.; Nendel, M.; Houk, K. N. *J. Am. Chem. Soc.* **1998**, *120*, 2989–2990. (b) Wudl, F.; Koutentis, P. A.; Weiz, A.; Ma, B.; Strassner, T.; Houk, K. N.; Khan, S. I. *Pure Appl. Chem.* **1999**, *71*, 295–302. (c) Riley, A. E.; Mitchell, G. W.; Koutentis, P. A.; Bendikov, M.; Kaszynski, P.; Wudl, F.; Tolbert, S. H. *Adv. Funct. Mater.* **2003**, *13*, 531–540.
- (4) Constantinides, C. P.; Koutentis, P. A.; Schatz, J. J. *J. Am. Chem. Soc.* **2004**, *126*, 16232–16241.

- (5) (a) Langer, P.; Bodtke, A.; Saleh, N. N. R.; Görls, H.; Schreiner, P. R. *Angew. Chem., Int. Ed.* **2005**, *44*, 5255–5259. (b) Miao, Q.; Nguyen, T. Q.; Someya, T.; Blanchet, G. B.; Nuckolls, C. *J. Am. Chem. Soc.* **2003**, *125*, 10284–10287.
- (6) 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.
- (7) Chen, H. Y.; Chao, I. *Chem. Phys. Chem.* **2006**, *7*, 2003–2007.
- (8) (a) Coropceanu, J. V.; Cornil, J.; da Silva, D. A.; Olivier, Y.; Silbey, R.; Bredas, J. L. *Chem. Rev.* **2007**, *107*, 926–952. (b) Anthony, E.; Facchetti, A.; Heeney, M.; Marder, S. R.; Zhan, X. *Adv. Mater.* **2010**, *22*, 3876–3892. (c) de Leeuw, D. M.; Simenon, M. M. J.; Brown, A. R.; Einerhand, R. E. F. *Synth. Met.* **1997**, *87*, 53–59.
- (9) (a) Zhang, Q.; Divayana, Y.; Xiao, J.; Wang, Z.; Tiekink, E. R. T.; Doung, H. M.; Zhang, H.; Boey, F.; Sun, X.; Wudl, F. *Chem.—Eur. J.* **2010**, *16*, 7422–7426. (b) Zhang, Q.; Xiao, J.; Yin, Z.; Duong, H. M.; Qiao, F.; Boey, F.; Hu, X.; Zhang, H.; Wudl, F. *Chem. Asian J.* **2011**, *6*, 856–862. (c) Xiao, J.; Divayana, Y.; Zhang, Q.; Doung, H. M.; Zhang, H.; Boey, F.; Sun, X.; Wudl, F. *J. Mater. Chem.* **2010**, *20*, 8167–8170. (d) Duong, H. M.; Bendikov, M.; Steiger, D.; Zhang, Q.; Sonmez, G.; Yamada, J.; Wudl, F. *Org. Lett.* **2003**, *5*, 4433–4436.
- (10) (a) Pascal, R. A., Jr. *Chem. Rev.* **2006**, *106*, 4809–4819. (b) Wu, Y. T.; Siegel, J. S. *Chem. Rev.* **2006**, *106*, 4843–4867. (c) Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028–5048.
- (11) Mateo-Alonso, A.; Kulisic, N.; Valenti, G.; Marcaccio, M.; Paolucci, F.; Prato, M. *Chem. Asian J.* **2010**, *5*, 482–485.
- (12) Pauling, L. *Acta Crystallogr.* **1980**, *B36*, 1898.
- (13) (a) Xiao, J.; Duong, H. M.; Liu, Y.; Shi, W.; Ji, L.; Li, G.; Li, S.; Liu, X.; Ma, J.; Wudl, F.; Zhang, Q. *Angew. Chem., Int. Ed.* **2012**, *51*, 10002/anie.201200949. (b) Xiao, J.; Liu, S.; Liu, Y.; Ji, L.; Liu, X.; Zhang, H.; Sun, X.; Zhang, Q. *Chem. Asian J.* **2012**, *7*, 561–564. (c) Xiao, J.; Malliakas, C. D.; Liu, L.; Zhou, F.; Li, G.; Su, H.; Kanatzidis, M. G.; Wudl, F.; Zhang, Q. *Chem. Asian J.* **2012**, *7*, 672.
- (14) (a) Madjar, A.; Herczfeld, P. R.; Paolella, A. *IEEE Trans. Microwave Theory Tech.* **1992**, *40*, 1681. (b) Romero, M. A.; Martinez, M. A. G.; Herczfeld, P. R. *IEEE Trans. Microwave Theory Tech.* **1996**, *44*, 2279–2287.
- (15) Noh, Y. Y.; Kim, D. Y.; Yase, K. *J. Appl. Phys.* **2005**, *98*, 074505–074511.
- (16) Forrest, S. R.; Thompson, M. E. *Chem. Rev.* **2007**, *107*, 923–925.
- (17) Tang, Q. X.; Li, L. Q.; Li, B. Y.; Xu, W.; Liu, Y. Q.; Hu, W. P.; Zhu, D. B. *Adv. Mater.* **2007**, *19*, 2624–2628.
- (18) Ji, H. X.; Hu, S. J.; Wan, L. J. *Chem. Commun.* **2008**, 2653.
- (19) Sze, S. M.; Ng, K. K. *Physics of Semiconductor Devices*, 3rd ed.; Wiley: New York, 2007.
- (20) Nunley, W.; Birtalan, D. *Optoelectronics: Infrared-Visible-Ultraviolet Devices and Applications*, 2nd ed.; CRC Press: Boca Raton, FL, 2009.