

# Variable Host–Guest Charge-Transfer Interactions in 1D Channels Formed in a Molecule-based Honeycomb Lattice of Phenazine Analogue of Triptycene

Ryo Ushiroguchi, Yoshiaki Shuku, Rie Suizu, and Kunio Awaga\*

Department of Chemistry and IRCCS, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan

*Honeycomb lattice, Charge transfer, Host–guest interaction*

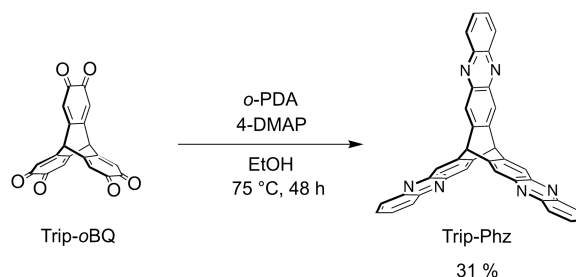
**ABSTRACT:** We synthesized a phenazine analogue of triptycene acceptor, Trip-Phz, and found a honeycomb network of Trip-Phz with a wide 1D channel running through it. The interior surface of this channel was covered by the  $\pi$  electrons of Trip-Phz. Even though there was no interaction between Trip-Phz and an organic donor, tetrathiafulvalene (TTF), in their solutions, the honeycomb crystals of Trip-Phz exhibited a host-guest charge-transfer (CT) interaction with TTF, specifically a reversible adsorption/desorption of TTF with the appearance/disappearance of a CT band.

Charge-transfer (CT) interaction between an organic donor and an acceptor has been studied extensively as a fundamental force in the formation of CT complexes and as a crucial process in organic electronics such as electrical conduction in dark and photo-induced charge separation.<sup>1–6</sup> Most solid-state CT interactions are ‘innate’, so that they take place in rigid donor-acceptor structures formed in the solids. However, we recently found an ‘acquired’ CT interaction induced by an insertion of organic donor molecules into a metal-organic framework (MOF) with an electron-accepting ligand.<sup>7</sup> Such an acquired host-guest CT interaction will be useful for molecular adsorption and separation, and for tuning the physical properties of the host frameworks.

Triptycene has a unique molecular structure consisting of polyhedral  $\pi$  conjugation planes whose normal axes form an angle of 60°. It was already demonstrated that intermolecular face-to-face overlaps between the  $\pi$  places in triptycene derivatives resulted in the formation of honeycomb lattices.<sup>8–13</sup> For example, we recently obtained a honeycomb lattice of the anion radical salt of Trip-*p*BQ, a *p*-benzoquinone analogue of triptycene, and calculated its exotic band structure, including the Dirac cones like those found in graphene, as well as flat bands, which were due to the orbital degeneracy caused by the high molecular symmetry ( $C_3$  axis).<sup>14</sup> Another feature of the honeycomb lattices of triptycene derivatives found so far was that the  $\pi$  conjugation planes were perpendicular to the 2D honeycomb networks so that, in the case of AA stacking of these networks, there were formations of 1D channels that perpendicular to the honeycomb lattices and whose interior surfaces were covered by  $\pi$  electrons. It is notable that this feature realized functional gas sorption and separation.<sup>15–18</sup>

In the present work, we synthesized a phenazine analogue of triptycene, Trip-Phz (see Scheme 1), having a weak electron-accepting ability. It was found that Trip-Phz molecules formed a honeycomb lattice due to face-to-face overlaps between the  $\pi$

places, and that the phenazine moiety’s ability to accept hydrogen bonds formed an AA stacking of these honeycomb lattices, forming a wide 1D channel with a diameter of 10 Å. Even though there was no CT interaction between Trip-Phz and the organic donor molecule, tetrathiafulvalene (TTF), in their solutions, the interior surfaces of the 1D channels in the Trip-Phz crystals exhibited a reversible host-guest CT interaction with the appearance of a strong CT band.

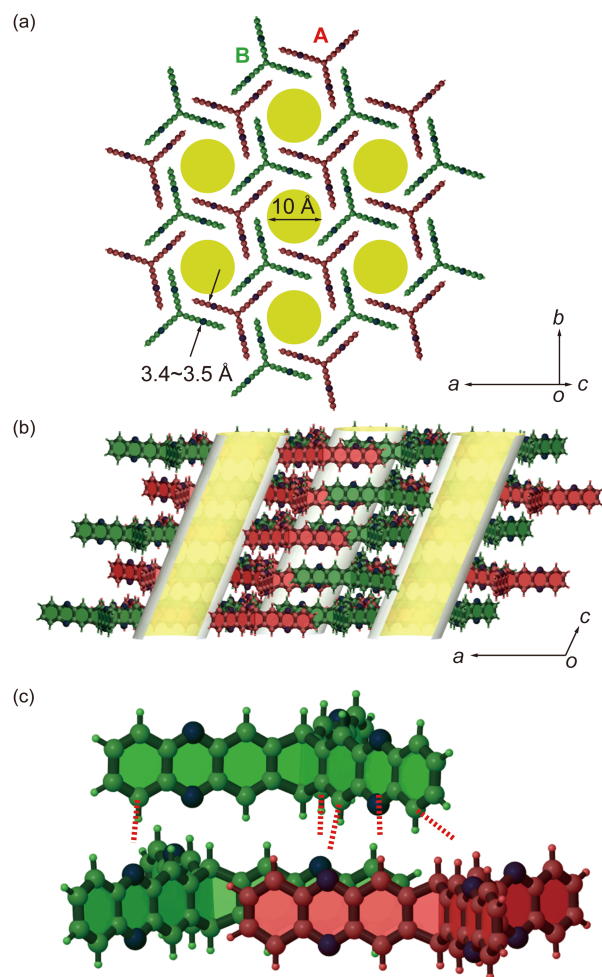


**Scheme 1** Synthesis of Trip-Phz

Trip-Phz was synthesized by the condensation reaction of 2,3,6,7,14,15-triptycenedehexaone (Trip-*o*BQ)<sup>19</sup> and *o*-phenylenediamine (*o*-PDA) in the presence of *N,N*-dimethylaminopyridine (4-DMAP) (Scheme 1). The crude product was purified by sublimation under reduced pressure to give pale yellow crystals. The crystal structure of the sublimed Trip-Phz, which is a close-packing structure, is shown in Figure S9. The molecular structure was also confirmed by NMR, MS, and elemental analyses.

Orange block crystals of THF@Trip-Phz were grown in THF/hexane solution by the vapor diffusion method. In air, these crystals lost crystallinity in a few minutes with the evaporation of the crystal solvents. X-ray single crystal analysis was performed at –150 °C for freshly prepared samples. The crystallographic data (Table S1) and the packing structure with THF molecules (Figure S6) are described in Supporting Information.

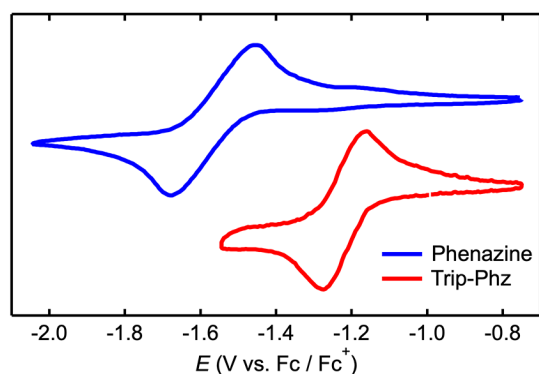
The crystal structure of THF@Trip-Phz belongs to the monoclinic space group, *Cc*. The unit cell consists of two crystallographically independent molecules, **A** and **B**, whose structures are nearly the same. As shown in Figure 1 (a), molecules **A** and **B** formed a honeycomb network with intermolecular  $\pi$ - $\pi$  overlaps between the phenazine moieties; in contrast, the sublimed Trip-Phz has no porous structure. The interplane distances of 3.44-3.51 Å are comparable to the sum of the van der Waals radii of carbon atoms (3.4 Å). The honeycomb structure possesses a void space with *ca.* 10 Å diameter and stacks along the *c* axis (Figure 1(b)). Figure 1(c) shows the interlayer contacts between the honeycomb layers. It is found that the phenazine moiety forms interlayer, intermolecular CH $\cdots$ N hydrogen bondings.<sup>20,21</sup> The red dotted lines in this Figure indicate these bonds with C $\cdots$ N distances of 3.23-3.59 Å. They form AA stacking, namely a nearly eclipsed overlap between the neighboring layers, which results in 1D channels, as shown in Figure 1(b). It is notable that the interior surfaces of the 1D channels in Trip-Phz are covered by  $\pi$  electrons, as shown in Figure S4.



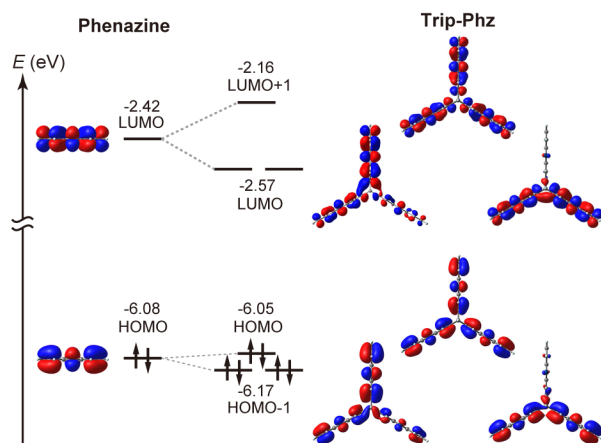
**Figure 1.** (a) Honeycomb lattice formed by Trip-Phz molecules, (b) 1D channel that runs through the honeycomb layers, and (c) interlayer CH $\cdots$ N hydrogen bonding. The molecules colored in red and green represent molecules **A** and **B**, respectively. THF molecules are omitted for clarity.

Cyclic voltammetry (CV) measurements were performed for the DMSO solution of Trip-Phz. The results are compared with the data on phenazine in Figure 2. Trip-Phz exhibits the first reduction potential at  $-1.22$  V (vs. Fc/Fc $^+$ ), while phenazine

does so at  $-1.56$  V. Figure 3 compares the molecular orbital energy levels of phenazine and Trip-Phz, as calculated by B3LYP/6-31G\*. It is clear that the HOMO of phenazine is split into three MOs in Trip-Phz, namely HOMO and doubly degenerated HOMO-1. The energies of HOMO and HOMO-1 of Trip-Phz are higher and lower than that of the HOMO of phenazine, because the HOMO and HOMO-1 of Trip-Phz are formed by bonding and antibonding overlaps between the HOMO of phenazine, respectively. The relationships between the LUMO of phenazine and the degenerated LUMO and LUMO+1 of Trip-Phz are the same as those for the HOMOs. The decrease in the first reduction potential for Trip-Phz, compared with that for phenazine, is well explained by the stabilization of the LUMO of Trip-Phz.



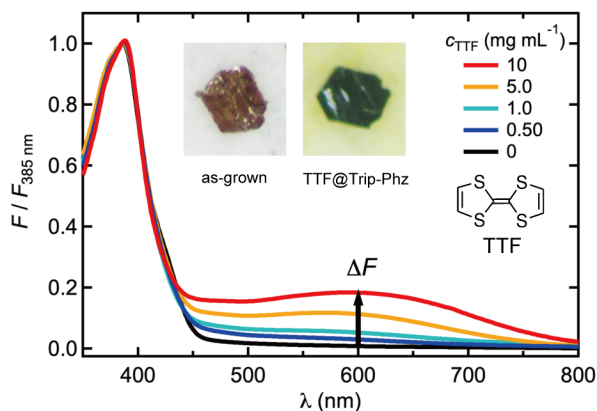
**Figure 2.** Cyclic voltammograms of phenazine and Trip-Phz in the DMSO solutions of 0.1 M tetrabutylammonium perchlorate with a scan rate of 50 mV s $^{-1}$ .



**Figure 3.** Frontier orbitals of phenazine and Trip-Phz.

The structural analysis of Trip-Phz revealed its wide 1D channels. In addition, the CV measurements and the MO calculation indicated the enhanced acceptor ability of this molecule. It was expected that the interior surfaces in these 1D channels would carry a  $\pi$ -acceptor ability. We then examined the intercalation of TTF,<sup>22</sup> a well-known donor molecule (HOMO level:  $-4.45$  eV calculated by B3LYP/6-31G\*). First, we mixed the THF solutions of Trip-Phz and TTF, but there was no appearance of a CT band (see Figure S5). Even so, we soaked single crystals of Trip-Phz in acetonitrile solution of TTF (10 mg mL $^{-1}$ ) at 45 °C, and found that, after one day, the crystals turned from orange to deep green (see the inset of Figure 4). Furthermore, the green

crystals returned to the original orange by soaking in pure acetonitrile for one day. Figure S8 shows the results of the SEM-EDX measurements for the orange and green crystals. It is clear that the green crystals contain sulfur atoms whereas the orange ones do not. This indicates a reversible insertion/desertion of TTF into/from the Trip-Phz crystals. Our X-ray structural analysis of the TTF-saturated crystals revealed that the lattice parameters were nearly the same as the values before the TTF doping (THF@Trip-Phz: monoclinic,  $Cc$  (#9),  $a = 34.290(2)$  Å,  $b = 20.0267(12)$  Å,  $c = 13.0816(7)$  Å,  $\beta = 112.256(3)^\circ$ ,  $V = 8314.1(8)$  Å<sup>3</sup>; TTF@Trip-Phz: monoclinic,  $Cc$  (#9),  $a = 34.38(2)$  Å,  $b = 19.838(12)$  Å,  $c = 13.165(9)$  Å,  $\beta = 112.317(11)^\circ$ ,  $V = 8306(9)$  Å<sup>3</sup>). This indicates that the TTF-doped molecules are accommodated in the 1D channels of Trip-Phz without affecting the framework of the honeycomb lattice, and the molecular plane of the TTF molecule faces to the cavity surface (Figure S7). However, we could not find all of the TTF molecules in this analysis, due to a significant positional and/or orientational disordering of TTF. To determine the number of inserted TTF molecules, we carried out an elemental analysis of the TTF-saturated crystals and estimated the molar ratio of Trip-Phz to TTF as 1 : 1.31 (see Supporting Information). This ratio means that one hexagon, formed by Trip-Phz molecules in the honeycomb lattice, accommodates nearly three TTF molecules. Note that it is still possible for the TTF-saturated crystals to include THF molecules.



**Figure 4.** Wavelength  $\lambda$  dependence of  $F$  for the TTF-doped Trip-Phz crystals prepared in TTF/methanol solutions of 0, 0.50, 1.0, 5.0, and 10 mg mL<sup>-1</sup>. The inset shows photographs of an as-grown Trip-Phz crystal and a TTF-introduced crystal.

We prepared TTF-doped Trip-Phz crystals with various concentrations, by soaking Trip-Phz crystals in TTF/methanol solutions of  $c_{\text{TTF}} = 0.1, 0.50, 1.0, 5.0,$  and  $10$  mg mL<sup>-1</sup>. We then performed solid-state UV-Vis-NIR reflection measurements of the powder samples (5 mg), which were dispersed into powder BaSO<sub>4</sub> (100 mg). The obtained relative reflectance to BaSO<sub>4</sub>,  $r$ , was transformed into the Kubelka–Munk function  $F$ ,<sup>23</sup>

$$F = \frac{(1-r)^2}{2r}, \quad (1)$$

which was proportional to absorbance. Figure 4 shows the wavelength  $\lambda$  dependence of  $F$ , in which the values of  $F$  are normalized by the value of the peak at 385 nm, which is caused by a strong absorption of the host molecule, Trip-Phz. The broad absorption around 600 nm gradually increases with an increase in the TTF doping level. The HOMO of TTF and the

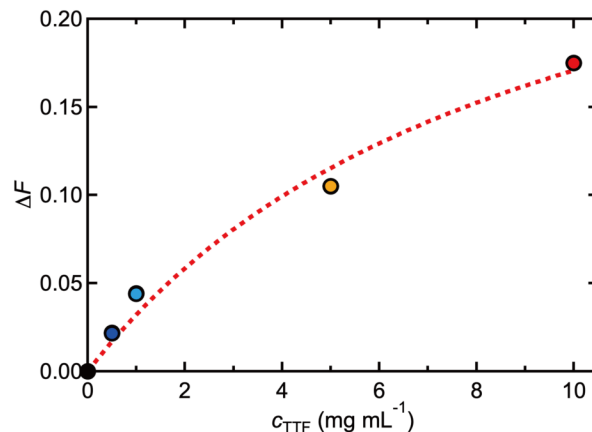
LUMO of Trip-Phz are located at  $-4.45$  eV and  $-2.57$  eV, respectively. Therefore, in the limit of weak CT interaction, we can expect the CT band at 1.88 eV. This corresponds to 660 nm. Therefore, it is assignable to the CT band between neutral Trip-Phz and TTF molecules.<sup>24</sup> This is supported by the fact that the TTF-doped green crystals are EPR-silent.

Trip-Phz honeycomb crystals exhibit CT interactions with TTF, though there is no CT interaction between Trip-Phz and TTF in their solutions. There are several possible interpretations. One is a steric effect of the Trip-Phz molecular skeleton, which hinders a one-to-one, face-to-face  $\pi$  overlap with TTF in their solutions. The extended  $\pi$  surfaces in the 1D channels might realize the interaction with TTF. Another possibility is the presence of a flat band at the bottom of the LUMO bands in the Trip-Phz honeycomb crystals (Figure S10).<sup>14</sup> Since the density of state of this band is huge, it might enhance the acceptor ability. In any case, the appearance of the CT band should be attributable to the coverage of the interior surfaces of the 1D channels in Trip-Phz by  $\pi$  electrons with acceptor properties.

Figure 5 shows the relationship between  $c_{\text{TTF}}$  and the difference in  $F/F_{385 \text{ nm}}$  at 600 nm,  $\Delta F$ , before and after TTF doping. The definition of  $\Delta F$  for the  $c_{\text{TTF}} = 10$  mg mL<sup>-1</sup> sample is shown in Figure 4. With an increase in  $c_{\text{TTF}}$ ,  $\Delta F$  quickly increases and becomes gradually saturated. It was found that this behavior can well fit Langmuir's equation,<sup>25</sup>

$$\Delta F = \frac{F_s K c_{\text{TTF}}}{1 + K c_{\text{TTF}}}, \quad (2)$$

where  $F_s$  is the saturation value of  $\Delta F$  and  $K$  is the adsorption equilibrium constant. The theoretical best fit was obtained with  $F_s = 0.33 \pm 0.08$  and  $K = 0.11 \pm 0.05$  mg<sup>-1</sup> mL. The effectiveness of this equation means that the interior of the 1D channels in Trip-Phz acts as an adsorption surface and that the adsorbed molecules, which are TTF, make a monolayer on it. This is quite consistent with the fact that this adsorption is caused by the donor–acceptor CT interaction. We previously found a host–guest CT interaction between a MOF host and inserted TTF molecules;<sup>2</sup> to our knowledge, however, the present material, TTF@Trip-Phz, is the first example to exhibit variable host–guest CT interactions.



**Figure 5.**  $\Delta F$  vs.  $c_{\text{TTF}}$  plots for TTF-doped Trip-Phz crystals prepared in TTF/methanol solutions of 0, 0.50, 1.0, 5.0, and 10 mg mL<sup>-1</sup>. The red broken curve indicates the theoretical best fit of Langmuir's equation (eq. (2)).

In summary, we synthesized a phenazine analogue of triptycene, Trip-Phz, having an extended  $\pi$  conjugation and an enhanced electron acceptor ability. It was found that van der Waals interactions between the aromatic moieties formed a honeycomb lattice of Trip-Phz and that  $\text{CH}\cdots\text{N}$  hydrogen bonding made a nearly eclipsed overlap between the honeycomb layers. As a result, this crystal involved wide 1D channels perpendicular to the honeycomb lattices, with diameters of *ca.* 10 Å, whose interior surfaces were covered by  $\pi$  electrons. We found reversible adsorption/desorption of TTF on/from these surfaces with the appearance/disappearance of the CT band, which well fit Langmuir's equation. Though the TTF molecules in Trip-Phz were in the neutral state, the present results strongly suggest a possible valence control, namely a band-filling control, for molecule-based honeycomb lattices.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental details (PDF)

Crystallographic data for sublimed-Trip-Phz and THF@Trip-Phz (CIF)

### Accession Codes

CCDC 1988017-1988018 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

## AUTHOR INFORMATION

### Corresponding Author

**Kunio Awaga** – Department of Chemistry and IRCCS, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan; orcid.org/0000-0002-2193-0747;

Email: [awaga.kunio@b.mbox.nagoya-u.ac.jp](mailto:awaga.kunio@b.mbox.nagoya-u.ac.jp)

### Authors

**Ryo Ushiroguchi** – Department of Chemistry and IRCCS, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan

**Yoshiaki Shuku** – Department of Chemistry and IRCCS, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan;

**Rie Suizu** – Department of Chemistry and IRCCS, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan; orcid.org/0000-0001-7632-2186

### Author Contributions

The manuscript was written through contributions of all of the authors.

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENT

The authors gratefully thank Dr. Kenji Yoza (Bruker Japan K.K.) for helpful discussions in X-ray structure analysis, and Dr. Kin-ichi Oyama (Chemical Instrumentation Faculty, Research Centre for Materials Science, Nagoya University) for technical assistance with ESI-MS and NMR measurements. This work was supported by JSPS KAKENHI Grant Numbers JP16H06353 (K. A.), JP18H04482 (K. A.), JP19K22167 (K. A.), JP19K15520 (Y. S.),

and JP20H02707 (R. S.). The single crystal X-ray diffraction measurements were performed at the Center for Analytical Instrumentation, Chiba University. Elemental analyses were carried out at the Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University.

## REFERENCES

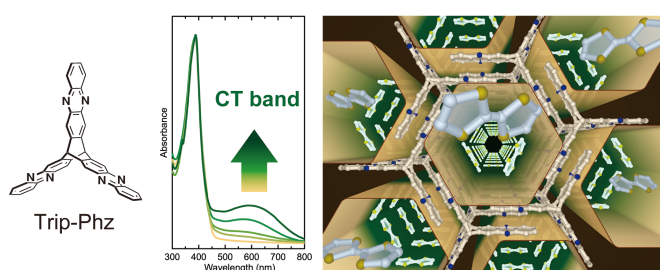
- (1) Horiuchi, S.; Tokura, Y. Organic ferroelectrics. *Nat. Mater.*, **2008**, *7*, 357-366.
- (2) Mori, T. Organic Charge-transfer Salts and the Component Molecules in Organic Transistors. *Chem. Lett.*, **2011**, *40*, 428-434.
- (3) Jiang, H.; Hu, P.; Ye, J.; Zhang, K. K.; Long, Y.; Hu, W.; Kloc, C. Tuning of the degree of charge transfer and the electronic properties in organic binary compounds by crystal engineering: a perspective. *J. Mater. Chem. C*, **2018**, *6*, 1884-1902.
- (4) Zhang, J.; Jin, J.; Xu, H.; Zhang, Q.; Huang, W. Recent progress on organic donor-acceptor complexes as active elements in organic field-effect transistors. *J. Mater. Chem. C*, **2018**, *6*, 3485-3498.
- (5) Huang, Y.; Wang, Z.; Chen, Z.; Zhang, Q. Organic Cocryystals: Beyond Electrical Conductivities and Field-Effect Transistors (FETs). *Angew. Chem. Int. Ed.*, **2019**, *58*, 9696-9711. (e) Jiang, H.; Hu, W. The Emergence of Organic Single-Crystal Electronics. *Angew. Chem. Int. Ed.*, **2020**, *59*, 1408-1428.
- (6) Wang, Z.; Zhang, Q. Organic Donor-Acceptor for Multiferroic Applications. *Asian J. Org. Chem.*, **2020**, *9*, 1-11.
- (7) Yamamoto, S.; Pirillo, J.; Hijikata, Y.; Zhang, Z.; Awaga, K. Nanopore-induced host-guest charge transfer phenomena in a metal-organic framework. *Chem. Sci.* **2018**, *9*, 3282-3289.
- (8) Bhola, R.; Payamyar, P.; Murray, D. J.; Kumar, B.; Teator, A. J.; Schmidt, M. U.; Hammer, S. M.; Saha, A.; Sakamoto, J.; Schülter, A. D.; King, B. T. A Two-Dimensional Polymer from the Anthracene Dimer and Triptycene Motifs. *J. Am. Chem. Soc.*, **2013**, *135*, 14134-14141.
- (9) Kissel, P.; Murray, D. J.; Wulfstange, W. J.; Catalano, V. J.; King, B. T. A nanoporous two-dimensional polymer by single-crystal to-single-crystal photopolymerization. *Nat. Chem.*, **2014**, *6*, 774-778.
- (10) Pulido, A.; Chen, L.; Kaczorowski, T.; Holden, D.; Little, M. A.; Chong, S. Y.; Slater, B. J.; McMahon, D. P.; Bonillo, B.; Stackhouse, C. J.; Stephenson, A.; Kane, C. M.; Clowes, R.; Hasell, T.; Cooper, A. I.; Day, G. M. Functional materials discovery using energy-structure-function maps. *Nature*, **2017**, *543*, 657-664.
- (11) Palmer, K. J.; Templeton, D. H. Crystal and Molecular structure of 1-Bromotriptycene  $\text{BrC}_{20}\text{H}_{13}$ . *Acta Cryst.*, **1968**, *B24*, 1048-1052.
- (12) Brynda, M.; Bernardinelli, G.; Dutan, C.; Geoffroy, M. Kinetic stabilization of Primary Hydrides of Main Group Elements. The Synthesis of an Air-Stable, Crystalline Arsine and Silane. *Inorg. Chem.*, **2003**, *42*, 6586-6588.
- (13) Betz, R.; McClelland, C.; Scheffer, A. 1-Iodotriptycene. *Acta Cryst.*, **2011**, *E67*, o2368.
- (14) Shuku, Y.; Mizuno, A.; Ushiroguchi, R.; Hyun, C. S.; Ryu, Y. J.; An, B.-K.; Kwon, J. E.; Park, S. Y.; Tsuchiizu, M.; Awaga, K. An exotic band structure of a supramolecular honeycomb lattice formed by a pancake  $\pi$ - $\pi$  interaction between triradical trianions of triptycene tribenzoquinone. *Chem. Comm.*, **2018**, *54*, 3815-3818.
- (15) Kohl, B.; Rominger, F.; Mastalerz, M. Rigid  $\pi$ -Extended Triptycenes via a Hexaketone Precursor. *Org. Lett.*, **2014**, *16*, 704-707.
- (16) Talipov, M. R.; Navale, T. S.; Rathore, R. The HOMO Nodal Arrangement in Polychromophoric Molecules and Assemblies Controls the Interchromophoric Electronic Coupling. *Angew. Chem. Int. Ed.*, **2015**, *54*, 14468-14472.
- (17) Kohl, B.; Bohnwagner, M. V.; Rominger, F.; Wadepohl, H.; Drew, A.; Mastalerz, M. Attractive Dispersion Interactions Versus Steric Repulsion of tert-Butyl groups in the Crystal Packing of a  $D_{3h}$ -Symmetric Tris(quinoxalinophenanthrophenazine). *Chem. Eur. J.*, **2016**, *22*, 646-655.
- (18) Prantl, E.; Kohl, B.; Ryvlin, D.; Biegger, P.; Wadepohl, H.; Rominger, F.; Bunz, U. H. F.; Mastalerz, M.; Waldvogel, S. R. Microporous Triptycene-Based Affinity Materials on Quartz Crystal Microbalances for Tracing of Illicit Compounds. *ChemPlusChem*, **2019**, *84*, 1239-1244.

- (19) Langis-Barsetti, S.; Maris, T.; Wuest, J. D. Triptycene 1,2-Quinones and Quinols: Permeable Crystalline Redox-Active Molecular Solids. *J. Org. Chem.* **2018**, *83*, 15426-15437.
- (20) Jankowski, W.; Gdaniec, M. The  $\beta$ -polymorph of phenazine. *Acta Cryst.*, **2002**, *C58*, o181-o182.
- (21) Berkovitch-Yellin, Z.; Leiserowitz, L. The Role Played by C-H $\cdots$ O and C-H $\cdots$ N Interactions in Determining Molecular Packing and Conformation. *Acta Cryst.* **1984**, *B40*, 159-165.
- (22) Bendikov, M.; Wudl, F.; Perepichka, D. F. Tetrathiafulvalenes, Oligoacenes, and Their Buckminsterfullerene Derivatives: The Brick and Mortar of Organic Electronics. *Chem. Rev.* **2004**, *104*, 4891-4945.
- (23) Wendlandt, W. W.; Hecht, H. G. *Reflectance spectroscopy*, Interscience Publishers, New York, 1966.
- (24) Torrance, J. B.; Vazquez, J. E.; Mayerle, J. J.; Lee, V. Y. Discovery of a Neutral-to-Ionic Phase Transition in Organic Materials. *Phys. Rev. Lett.*, **1981** *46*, 253-257.
- (25) Langmuir, I. The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum. *J. Am. Chem. Soc.*, **1918**, *40*, 1361-1403.

"For Table of Contents Use Only"

## Variable Host–Guest Charge-Transfer Interactions in 1D Channels Formed in a Molecule-based Honeycomb Lattice of Phenazine Analogue of Triptycene

Ryo Ushiroguchi, Yoshiaki Shuku, Rie Suizu, and Kunio Awaga



A phenazine analogue of triptycene, Trip-Phz, formed a honeycomb lattice with wide 1D channels. The interior surface of these channels was covered by the  $\pi$  electrons. Even though there was no interaction between Trip-Phz and an organic donor, tetrathiafulvalene, in their solutions, the honeycomb crystals of Trip-Phz realized a reversible adsorption/desorption of tetrathiafulvalene with the appearance/disappearance of a charge-transfer band.

---