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Layered donor-acceptor-acceptor arrangement in complex of molecular tweezer based on dioxa[2.2]orthocyclophane

Hirotaka Kurebayashi, Takeharu Haino and Yoshimasa Fukazawa *

Department of Chemistry, Graduate School of Science, Hiroshima University, Higashi-Hiroshima 739-8526, Japan

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Abstract

Flexible molecular receptors having three aromatic chromophores can bind electron deficient π -system such as TCNQ and TCNB with both face-to-face and face-to-edge interactions. The receptors have tweezer-type conformations when a guest was trapped within their cavities. Sandwich-type donor-acceptor-acceptor (DAA) arrangement was realized in the crystalline supramolecular complex. © 2000 Elsevier Science Ltd. All rights reserved.

Noncovalent interaction between aromatic rings and neutral planar molecules plays an important role both in the structure and property of supramolecular complexes. Molecular tweezers,¹ containing two aromatic chromophores connected by a spacer are suitable receptors for planar, π -electron guests since they can hold the guest with the two aromatic arms through the π -stacking interactions.² Efficient binding of a π -electron acceptor can be attained by the two aromatic binding arms of the host forming a charge transfer type interaction.³ Rigid tweezers,⁴ having a preorganized face-to-face arrangement of the two aromatic chromophores are known to be favorable for strong binding of a guest. Flexible tweezer,⁵ on the other hand, has the adaptability for the variation of guests, though there should be an entropic cost for the face-to-face orientation of the two arms. In a previous paper,⁶ we reported that the flexible tweezer (1) based on dioxa[2.2]orthocyclophane⁷ can bind π -electron deficient guests such as tetracyanoquinodimethane (TCNQ), pyromellitic dianhydride (PDA), and tetracyanobenzene (TCNB) effectively to form a 1: 1 complex both in solution and in the crystalline state (1·TCNQ). We also reported that if one of the two binding chromophores was as small as a benzene ring, a 1:1 complex formation was not observed in the crystalline state (2·TCNQ), hence, the cavity size of the tweezer plays an important role in effective binding.

^{*} Corresponding author.

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In a continued effort to understand the detailed mechanism of guest binding, we have found that the replacement of the benzene ring of the binding arm in 2 by benzoic acid ester resulted in the effective binding of the π -electron deficient guest with the tweezer-type conformation in the crystalline state. In this paper, we report on the detailed molecular structures of these supramolecular complexes.

The molecular receptors **3** and **4** were synthesized by a similar route as those of **1** and **2** (Scheme 1). Successive coupling of 1,2,4,5-tetrakis(bromomethyl)benzene **5** with 9,10-dihydroxyphenanthrene **6** and the corresponding aromatic diols in the presence of Cs_2CO_3 in acetone gave the corresponding receptors **3** or **4**.



Scheme 1. (a) 1,2,4,5-Tetrakis(bromomethyl)benzene, Cs_2CO_3 , acetone, 20%; (b) for **3**: methyl-3,4-dihydroxybenzoate, Cs_2CO_3 , acetone, 89% for **4**: dimethyl-4,5-dihydroxyphthalate, Cs_2CO_3 , acetone, 81%

The structures of the supramolecular complexes were examined by X-ray crystallography⁸ and ORTEP drawings of these complexes are shown in Fig. 1. As can be seen clearly, host **3** has a tweezer-type conformation with face-to-face arrangement of the two terminal aromatic rings. They lie parallel to each other and the distance between them is 6.78 Å. The guest (TCNQ) resides in the cavity of the host and has both the stacking interaction between the two terminal aromatic chromophores and the edge-to-face interaction⁹ with the central aromatic ring of the host. The guest is parallel to each of the two aromatic chromophores of the host. The distances between the two chromophores and the guest are 3.56 (from methyl benzoate side) and 3.37 Å (from phenanthrene side), respectively. The two hydrogens of the guest are pointing towards the central aromatic ring of the host at distances of 2.78 and 3.03 Å, suggesting a favorable edge-to-face interaction. The ester group of **3** lies within the plane of the benzene ring to which it attached. It might have the role of expanding the cavity size in which the guest resides in order to increase the contact area between the host and guest.

Due to the heavy repulsion between them, the two ester groups in 4 cannot lie within the aromatic plane to which they are attached. In spite of this nonplanar aromatic chromophore, 4 can grasp an electron deficient guest (TCNB) in the crystalline state. The host has also a tweezer-type conformation with a face-to-face arrangement of the two terminal aromatic rings. These aromatic rings lie parallel to each other and the distance between them is 7.10 Å, slightly longer than the corresponding value for $3 \cdot \text{TCNQ}$, reflecting the nonplanar aromatic chromophore. The structural characteristics of $4 \cdot \text{TCNB}$ are very similar to those



Fig. 1. ORTEP drawings of (a) 3. TCNQ and (b) 4. TCNB

in $3 \cdot \text{TCNQ}$ except for the longer interplanar distances between the nonplanar chromophore and the guest and between the above mentioned terminal chromophore. The structural details of these complexes are summarized together with those of $1 \cdot \text{TCNQ}$ for comparison (Table 1).

Table 1
Interplanar distances (Å) and angles (Å) of supramolecular complexes

R	A-D	C-D	A-C	<a•d< th=""><th><c•d< th=""><th><a•b< th=""><th><b•c< th=""></b•c<></th></a•b<></th></c•d<></th></a•d<>	<c•d< th=""><th><a•b< th=""><th><b•c< th=""></b•c<></th></a•b<></th></c•d<>	<a•b< th=""><th><b•c< th=""></b•c<></th></a•b<>	<b•c< th=""></b•c<>
1•TCNQ	3.24	3.31	6.54	1.7	2.7	91.6	91.5
D 3•TCNQ	3.37	3.56	6.78	2.8	9.3	86.9	85.8
4•TCNB	3.45	3.71	7.10	4.1	12.2	93.0	101.0

Apart from their role in expanding the contact area between the host and guest, the electron withdrawing ester groups change the electronic character of the terminal aromatic ring from donating to accepting. The change of the electronic character can be clearly shown with the semi-empirical molecular orbital calculation (PM3) for **7** (Table 2). Thus, the sandwich arrangement of the three components, phenanthrene, TCNQ, and methyl benzoate produces donor–acceptor–acceptor (DAA) stacking.¹⁰

Table 2
HOMO and LUMO energy (eV) of 7

		R ₁ =R ₂ =H	R ₁ =CO ₂ Me R ₂ =H	R ₁ =CO ₂ Me R ₂ =CO2Me
R_2	НОМО	-9.07	-9.34	-9.87
	LUMO	0.00	-0.53	-0.82

A simple consideration based on the perturbation theory¹¹ suggested the decrease of the LUMO energy level of acceptor guest by the interaction between the terminal aromatic ester moiety, since the LUMO of the latter is higher in energy (Table 2) than the former (TCNQ (-3.07 eV), TCNB (-2.33 eV)).

The decrease of the guest LUMO facilitates the charge transfer interaction between the other terminal chromophore (phenanthrene). Thus, the aromatic ester terminal plays an important role not only in the increase of the contact area with the guest but also in facilitating the charge transfer interaction.

In conclusion, we demonstrated sandwich-type arrangement of donor-acceptor-acceptor (DAA) both in $3 \cdot \text{TCNQ}$ and $4 \cdot \text{TCNB}$ in the crystalline state. It is a clear demonstration that not only the layered arrangement of the donor-acceptor-donor (DAD) but also DAA sandwich-type arrangement gives stable intermolecular complexes in the crystalline state.

References

- (a) Zimmerman, S. C. In *Bioorganic Chemistry Frontiers*; Dugas, H., Ed.; Springer-Verlag: Berline, Heidelberg, 1991; Vol. 2, pp. 33–71. (b) Chen, C.-W.; Whitlock, H. W. J. Am. Chem. Soc. **1978**, 100, 4921–4922.
- (a) Hunter, C. A.; Sanders, J. K. M. J. Am. Chem. Soc. 1990, 112, 5525–5534. (b) Adams, H.; Carver, F. J.; Hunter, C. A.; Morales, J. C.; Seward, E. M. Angew. Chem.. Int. Ed. Engl. 1996, 35, 1542–1544. (c) Hamilton, A. D.; Van Eugen, D. J. Am. Chem. Soc. 1987, 109, 5035–5036.
- 3. Foster, R. Organic Charge-Transfer Complexes; Academic Press: New York, 1969.
- 4. (a) Zimmerman, S. C.; VanZyl, C. M.; Hamilton, G. S. J. Am. Chem. Soc. 1989, 111, 1373–1381. (b) Harmata, M.; Barnes, C. L. Tetrahedron Lett. 1990, 31, 1825–1828; ibid J. Am. Chem. Soc. 1990, 112, 5655–5657. (c) Sijbesma, R. B.; Kentgens, A. P. M.; Lutz, E. T. G.; van der Maas, J. H.; Nolte, R. J. M. J. Am. Chem. Soc. 1993, 115, 8999–9005 (d) D'Souza, L. J.; Maitra, U. J. Org. Chem. 1996, 61, 9494–9502. (e) Mink, D.; Deslongchamps, G. Tetrahedron Lett. 1996, 37, 7035–7038.
- (a) Allwood, B. L.; Colguhoun, H. M.; Doughty, S. M.; Kohuke, F. H.; Slawin, A. M. Z.; Stoddart, J. F.; Williams, D. J.; Zarzycki, R.; J. Chem. Soc., Chem. Commun. 1987, 1054–1058. (b) Lamsa, M.; Suorasa, T.; Pursiainen, J.; Huuskonen, J.; Rissanen, K. J. Chem. Soc., Chem. Commun. 1996, 1443–1444.
- 6. Kurebayashi, H.; Sakaguchi, M.; Okajima, T.; Usui, S.; Haino, T.; Fukazawa, Y. Tetrahedron Lett. 1999, 40, 5545–5548.
- 7. (a) Kurebayashi, H.; Mine, T.; Harada, K.; Usui, S.; Okajima, T.; Fukazawa, Y. *Tetrahedron* **1998**, *54*, 13495–13504. (b) Kleinpeter, E.; Gabler, M.; Schroth, W. *Monatshefte Chem.* **1988**, *119*, 233–246.
- 8. X-Ray structural analysis of 3·TCNQ and 4·TCNB: MXC-3 diffractometer, graphite monochromated Mo-Kα, structure solved by direct method and refined with the least-squares method against F (Sir97). Complex 3₂·TCNQ₃ complex: brown prisms, space group *Pb2₁a*, orthorhombic, *a*=15.557(1), *b*=17.218(1), *c*=29.998(1) Å, *V*=8035.3(1) Å³, *Z*=4, 8729 measured, 8000 were observed (*F*>3σ (*F*)). *R*=0.089, *wR*²=0.082; Complex 4₂·TCNB₃: orange prisms, space group P2₁/c, monoclinic, *a*=16.341(1), *b*=13.104(1), *c*=18.190(1) Å, *b*=93.30(2)°, *V*=3904(1) Å³, *Z*=2, 9897 measured, 7482 were observed (*F*>3σ (*F*)). *R*=0.072, *wR*²=0.065.
- (a) Rebek Jr., J. Science 1987, 235, 1478–1484. (b) Jorgensen, W. L.; Severance, D. L. J. Am. Chem. Soc. 1990, 112, 4768–4774. (c) Hobza, P.; Selzle, H. L.; Schlag, E. W. J. Am. Chem. Soc. 1994, 116, 3500–3506. (d) Kim, E.; Paliwal, S.; Wilcox, C. S. J. Am. Chem. Soc. 1998, 120, 11192–11193.
- 10. Only a few sandwich-type layered complexes deviating from a 1:1 (D:A) have been reported. See, for an example of DAAAD: Harms, R.; Keller, H. J.; Nothe, D.; Wehe, D. *Acta Cryst.* **1982**, *B38*, 2838–2841.
- 11. Fleming, I. Frontier Orbitals and Organic Chemical Reactions; John Wiley: New York 1976; pp. 23–32.