Pergamon

Tetrahedron Letters 39 (1998) 5155–5158

TETRAHEDRON
LETTERS

Noncovalent Synthesis of Donor/Acceptor Stacks

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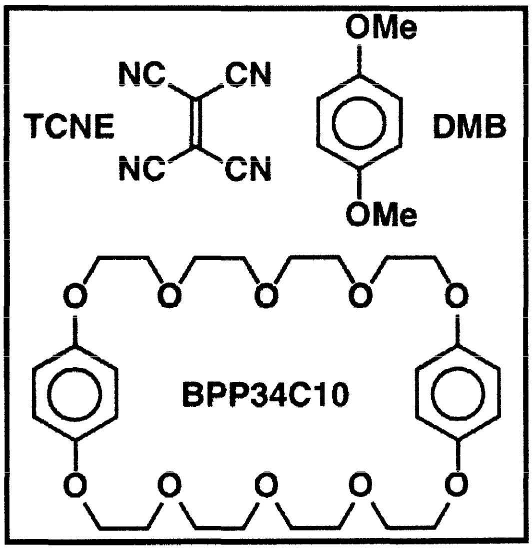
Received 18 March 1998; revised 5 May 1998; accepted 7 May 1998

Abstract: Supramolecular arrays composed of alternating tetracyanoethylene acceptors (A) and 1,4-dioxybenzene-based donors (D) self-assemble spontaneously in the solid state. Infinite one-dimensional [···A···D···A···D···] stacks are formed by co-crystallizing tetracyanoethylene and 1,4-dimethoxybenzene. When bis-*p*-phenylene-34-crown-10, possessing two 1,4-dioxybenzene donors (D–D) bridged by polyether chains, is employed, infinite one-dimensional [···A···D–D···A···D–D···] arrays are formed with the cavities of macrocyclic polyethers of adjacent stacks perfectly in register to afford channels — occupied by MeCN molecules — along one crystallographic direction.

Crystal engineering[1,2] offers the opportunity to design and construct solids with defined architectures from relatively simple starting components. Cooperative noncovalent bonding interactions control the nucleation of supramolecular assemblies which grow into well-defined supramolecular arrays and finally into a macroscopic aggregate — namely, a crystal. Understanding the fundamental principles of supramolecular synthesis[3] is, thus, central to the development of crystal engineering and identifying appropriate *tectons*[4] capable of sustaining hydrogen bonding, π–π stacking, and/or metal coordination can be equated to devising new chemical reactions in classical covalent synthesis. In our quest[3c] for supramolecular synthons suitable for the construction of self-assembling supramolecular arrays, we have focused our attention on tetracyanoethylene (TCNE). This simple molecule is a unique polydentate non-chelating ligand which can exist in three different redox states and which can coordinate up to four metal centers *via* several different bonding modes.[5] In addition, TCNE sustains π–π stacking interactions with a number of organic π-systems, as a result of a combination of electrostatic and charge-transfer interactions.[6] In previous work,[7] we have employed π–π stacking interactions, between dioxyarene donors and bipyridinium acceptors, to assist in the template-directed syntheses of mechanically-interlocked



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PII: S0040-4039(98)00985-X

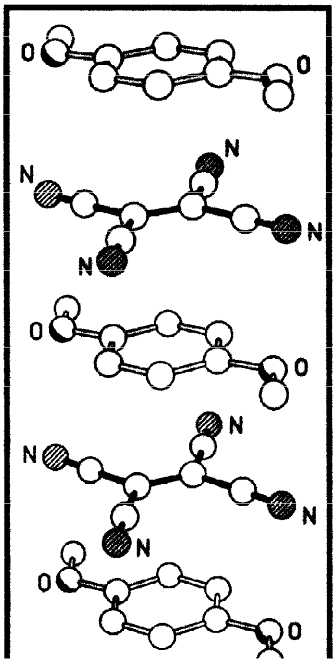

Figure 1. Ball-and-stick representation of one of the donor/acceptor stacks formed in the solid state by DMB and TCNE.

compounds and to self-assemble supramolecular arrays in the solid state. As a logical development of this previous work, we have investigated the possibility of engineering and self-assembling supramolecular arrays composed of TCNE and 1,4-dioxybenzene-based *tectons*. Here, we report the association constants of the 1:1 complexes formed between TCNE and 1,4-dimethoxybenzene (DMB) and between TCNE and bis-*p*-phenylene-34-crown-10 (BPP34C10) in solution as well as the single crystal X-ray analyses of both 1:1 complexes.

On combining equimolar amounts of TCNE and DMB in CH_2Cl_2, a dark blue color develops immediately, suggesting complex fomation.[8,9] Since both TCNE and DMB can sustain π–π stacking interactions with both their faces, the formation of oligomeric [···D···A···D···A···] complexes as well as a discrete [D···A] complex can be envisaged in solution. In order to unravel the nature of the supramolecular species formed in solution, we have performed absorption UV-Vis spectroscopic studies both in CH_2Cl_2 and in MeCN. We have employed the dilution and the continuous variation procedures[10] by monitoring the change in the absorbance of the charge-transfer bands (CH_2Cl_2, λ_{max} = 641 nm; MeCN, λ_{max} = 594 nm), observed in the UV-Vis spectra, upon changing the concentration of the solutes.[11] Both methodologies point to the exclusive formation of a 1:1 complex between TCNE and DMB with association constant (K_a) values of 7 ± 2 and 4 ± 2 M^{-1} in CH_2Cl_2 and in MeCN, respectively, at 25°C. Thus, *in solution, oligomeric [···D···A···D···A···] complexes are not formed.* By contrast, the X-ray analysis[12] of single crystals, grown after the slow liquid-liquid diffusion of hexane into an equimolar solution of TCNE and DMB in $CHCl_3$, revealed (**Figure 1**) *the formation of infinite one-dimensional [···D···A···D···A···] stacks in the solid state.* DMB and TCNE molecules are oriented[13] with their mean planes parallel to each other with interplanar and [centroid···centroid] separations of 3.28 and 3.29 Å, respectively, and a [centroid···centroid] off-set of 0.23 Å. The angle subtended by the [O···O] axis of DMB and the [C=C] axis of TCNE is 51°. In each TCNE molecule, two centrosymmetrically-related nitrogen atoms are sandwiched each between two oxygen atoms of different DMB molecules ([O···N] 3.31 and 3.28 Å, [O···N···O] 172°). No significant interactions between adjacent stacks in the crystal were observed.

Encouraged by these results, we considered the possibility of complex formation between TCNE and BPP34C10: a macrocycle which incorporates two 1,4-dioxybenzene donors bridged by two polyether chains.[14] On mixing equimolar amounts of TCNE and BPP34C10 in either CH_2Cl_2 or MeCN, a dark blue color develops immediately, indicating

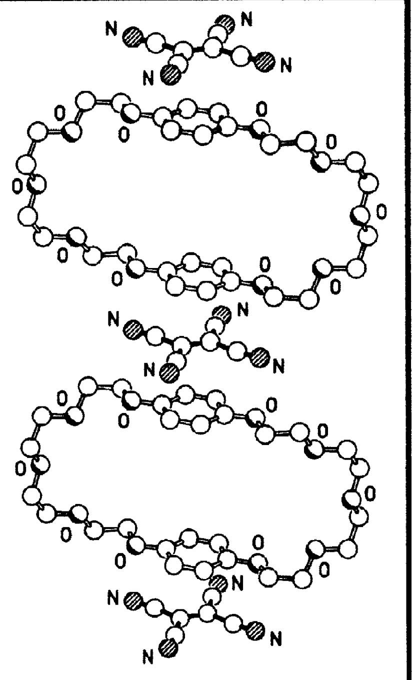

Figure 2. Ball-and-stick representation of one of the donor/acceptor stacks formed in the solid state by BPP34C10 and TCNE.

complex formation. As described previously in the case of the TCNE•DMB complex, in order to investigate the stoichiometry and the stability of the supramolecular species formed in solution, we have performed absorption UV-Vis spectroscopic studies. As before, using both the dilution and the continuous variation approaches, we have monitored the change in the absorbance of the charge-transfer bands (CH_2Cl_2, λ_{max} = 650 nm; MeCN, λ_{max} = 575 nm), observed in the UV-Vis spectra, upon altering the concentration of the solutes. Once again in solution, only a 1:1 complex could be detected in solution: *no supramolecular oligomers are formed.* However, the K_a values (65 ± 13 and 19 ± 6 M^{-1} in CH_2Cl_2 and in MeCN, respectively, at 25°C), determined for the 1:1 complex formed between TCNE and BPP34C10, are significantly higher than those determined in the case of the TCNE•DMB complex. Presumably, inclusion of the TCNE acceptor inside the macrocyclic cavity of BPP34C10 occurs in solution, affording a [D···A···D] complex rather than a much weaker [D···A] complex, as in the case of DMB. X-Ray analysis[15] of single crystals, grown after cooling an equimolar solution of TCNE and BPP34C10 in MeCN, has revealed (**Figure 2**), however, that *in the solid state, the TCNE acceptor is not included within the cavity of the BPP34C10 macrocycle*: instead, the cavity is filled by two MeCN molecules. Each TCNE molecule is sandwiched between two 1,4-dioxybenzene rings of lattice-translated BPP34C10 macrocycles with identical interplanar and [centroid···centroid] separations (3.22 Å), the two components being positioned on/about crystallographic inversion centers. While no significant [centroid···centroid] off-set is observed between the TCNE acceptors and the sandwiching aromatic units, the two 1,4-dioxybenzene rings of each BPP34C10 macrocycle are slightly sheared with a [centroid···centroid] off-set of 0.79 Å and interplanar and [centroid···centroid] separations of 6.84 and 6.89 Å, respectively. The angle subtended by the [C=C] axis of TCNE and the [O···O] axes of the sandwiching 1,4-dioxybenzene rings is 36°. In each TCNE molecule, two centrosymmetrically-related nitrogen atoms are sandwiched each between two oxygen atoms of different 1,4-dioxybenzene rings ([O···N] 3.31 and 3.21 Å, [O···N···O] 159°). The TCNE•BPP34C10 stacks are aligned in the crystal with the cavities of adjacent BPP34C10 macrocycles perfectly in register, forming channels along the crystallographic *a* direction.

The noncovalent synthesis of well-defined supramolecular arrays has been realized in the solid state, starting from commercially available (TCNE and DMB) and easily accessible (BPP34C10) *tectons*. By exploiting the versatility of TCNE, as both a π-acceptor and a multidentate ligand for transition metals, and by employing complementary dioxyarene π-donors in combination with the appropriate metal centers, new and more complex supramolecular arrays with engineered electrochemical, magnetic, and/or photochemical properties could be constructed in the solid state. This is an objective of our current research in this area.

Acknowledgments. This research work was supported by the Engineering and Physical Sciences Research Council in the UK.

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11. TCNE was purified by crystallization from PhCl followed by sublimation. DMB was purified by crystallization from PhCl.
12. Crystal data for the complex TCNE•DMB: $C_{14}H_{10}N_4O_2$, M = 266.26, triclinic, space group = $P\bar{1}$, a = 6.5731(4), b = 6.7966(6), c = 8.1064(4) Å, α = 96.847(6), β = 105.010(4), γ = 103.021(6)°, V = 334.68(4) Å^3, Z = 1, ρ_{calc} = 1.321 g cm^{-3}, $\mu(Cu_{K\alpha})$ = 7.66 cm^{-1}, $F(000)$ = 138, T = 223 K. 974 Independent reflections were measured on a Siemens P4/PC diffractometer with $Cu_{K\alpha}$ radiation (graphite monochromator) using ω-scans. The structure was solved by direct methods. Refinement was by full matrix least-squares based on F^2 to give R_1 = 0.059, wR_2 = 0.160 for 723 independent observed reflections [$I > 2\sigma(I)$, $2\theta \le 120°$] and 91 parameters.
13. The single crystal X-ray analysis of a 1:1 complex formed between TCNE and 5,8-dimethoxy-2,11-dithia[3.3]paracyclophane — *i.e.*, a cyclophane incorporating, in one of its two *para*-phenylene rings, a pair of methoxyl substituents that are *para* to each other — shows a similar relative orientation of the TCNE acceptor and the *para*-dimethoxy-substituted donor. The mean planes of the two units are parallel to each other with interplanar and [centroid···centroid] separations of 3.15 and 3.10 Å, respectively. The angle subtended by the [O···O] axis of the donor and the [C=C] axis of the acceptor is 35°. See: Cohen-Addad, C.; Consigny, M.; D'Assenza, G., Baret, P. *Acta Cryst.* **1988**, *C44*, 1924–1926.
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15. Crystal data for the complex TCNE•BPP34C10: $C_{34}H_{40}N_4O_{10}$•2MeCN•0.5H_2O, M = 755.82, triclinic, space group = $P\bar{1}$, a = 8.586(2), b = 11.150(3), c = 13.028(4) Å, α = 67.96(2), β = 72.74(2), γ = 86.42(2)°, V = 1102.4(5) Å^3, Z = 1, ρ_{calc} = 1.139 g cm^{-3}, $\mu(Cu_{K\alpha})$ = 6.96 cm^{-1}, $F(000)$ = 401, T = 293 K. 2769 Independent reflections were measured on a Siemens P4/PC diffractometer with $Cu_{K\alpha}$ radiation (graphite monochromator) using ω-scans. The structure was solved by direct methods. Refinement was by full matrix least-squares based on F^2 to give R_1 = 0.094, wR_2 = 0.271 for 2209 independent observed reflections [$I > 2\sigma(I)$, $2\theta \le 110°$] and 249 parameters.