

Electrostatic Enforcement in the Synthesis of Low Dimensional
Charge Transfer Materials from Ruthenium Complexes

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Literature Seminar

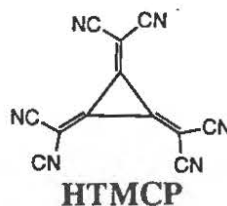
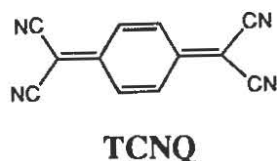
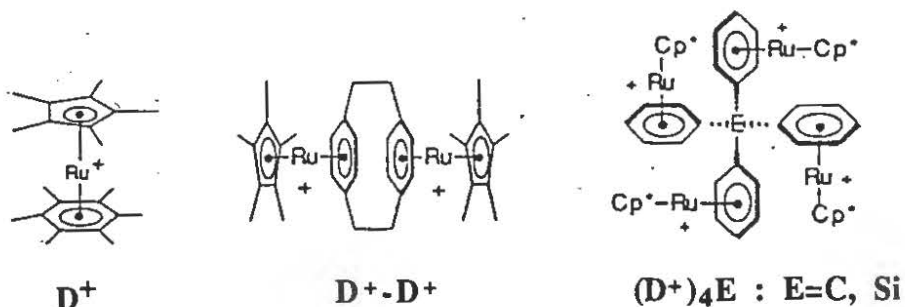
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One of the most challenging obstacles in the synthesis of solid state materials is the difficulty in obtaining a desired lattice structure. One commonly used approach to engineer a solid is modification of a previously determined structure. Substitution of atoms within a solid lattice and inclusion of molecules into a layered framework are good examples of this approach [1].

In one-dimensional molecular solids, the stacking of flat molecules often allows some rational control of lattice structure [2]. Since the synthesis of oxygen-bridged germanium phthalocyanines by Kenney in 1960 [3], the study of co-facially linked, partially oxidized metallocycles such as $\{[M(Pc)O]I_x\}_n$ ($M = Si, Ge, Sb$) and $Ni(Pc)I$ [3] has been carried out. Interest in one-dimensional solids was heightened with the discovery of the organic conductor TTF-TCNQ (TTF = tetrathiofulvalene, TCNQ = tetracyanoquinodimethane) in 1973 [4], followed by the discovery of superconductivity in $(TMTSF)_2X$ (TMTSF = tetramethyltetraselenafulvalene; $X = PF_6^-, ClO_4^-, AsF_6^-$) [5].

In 1962, ferrocene was reported to form a 1:2 charge transfer complex with the organic acceptor TCNQ which exhibits conductivity at room temperature [6]. Since then, charge transfer complexes between organometallic donors and organic acceptors have shown interesting physical and chemical properties that involve crystal packing, donor-acceptor interactions, stoichiometry, and conductivity [7].

Very recently, one approach to controlling the structures of one-dimensional organometallic charge transfer complexes has been carried out by taking advantage of electrostatic interactions between organometallic cations and organic anions. Polycationic ruthenium complexes with specific geometries and localized charges such as $[Cp^*Ru(\eta^6-C_6Me_6)^+](D^+)$, $[(Cp^*Ru)_2-(\eta^6, \eta^6-[2_2](1,4)cyclophane)^{2+}](D^+-D^+)$, and $[(Cp^*Ru)_4(\eta^6-C_6H_5)_4E^{4+}](D^+)_4E$: $E = C, Si$) have been synthesized as cationic building blocks. TCNQ and HTMCP (hexacyanotrimethylenecyclopropane) have been used as organic π -acceptor anions which tend to align in linear chains. The reaction between D^+ and $TCNQ^-$ results in $[D^+][TCNQ^-]$ (1) which forms a paramagnetic one-dimensional mixed stack of D^+ cations and $TCNQ^-$ anions. Compounds of stoichiometry $[D^+-D^+][TCNQ^-]_x$ (2, $x = 2$; 3, $x = 4$) have been synthesized by electrochemical reaction between the D^+-D^+ dication and the $TCNQ^-$ anion. Nonconducting 2 possesses linear chains with a $(D^+-D^+)(A^-A^-)(D^+-D^+)(A^-A^-)$ motif. In contrast, conducting 3 possesses two crystallographically independent tetrameric TCNQ stacks parallel to the long axis of the cations. The solid structures of the nonconducting charge-transfer salts $[D^+-D^+][HTMCP^-]_2$ (4) and $[(D^+)_4E][HTMCP^-]_4$ (5, $E = C$; 6, $E = Si$) exhibit linear chains of HTMCP⁻ anions. For 4, the anion stacking axis is parallel to the long axis of the dications, whereas 5 and 6 have mutually orthogonal anion stacks that come from electrostatic enforcement by two orthogonal pairs of cationic centers in the tetracations [8].



References

1. (a) Wells, A. F. *Structural Inorganic Chemistry*; Oxford University Press: Oxford, 1984.
 (b) West, A. R. *Solid State Chemistry and Its Application*; John Wiley & Sons: New York, 1984.
2. *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum Press: New York, 1981-1983, vol. 1-3.
3. (a) Joyner, R. D.; Kenney, M. E., "Germanium Phthalocyanines," *J. Am. Chem. Soc.* **1960**, *82*, 5790.
 (b) Schoch, K. F., Jr.; Kundalkar, B. R.; Marks, T. J., "Conductive Polymers Consisting of Partially Oxidized, Face-to-Face Linked Metallomacrocycles," *J. Am. Chem. Soc.* **1979**, *101*, 7071.
4. Ferraris, J.; Cowan, D. O.; Walatka, V.; Perlstein, J. H., "Electron Transfer in a New Highly Conducting Donor-Acceptor Complex," *J. Am. Chem. Soc.* **1973**, *95*, 948.
5. Jerome, D.; Schutz, H. J., "Organic Conductors and Superconductors," *Adv. Phys.* **1982**, *31*, 299.
6. Melby, L. R.; Harder, R. J.; Hertler, W. L.; Mahler, W.; Benson, R. E.; Mochel, W. E., "Substituted Quinodimethanes. II. Anion-radical Derivatives and Complexes of 7,7,8,8-Tetracyanoquinodimethane," *J. Am. Chem. Soc.* **1962**, *84*, 3374.
7. (a) Reis, A. H., Jr.; Preston, L. D.; Williams, J. M.; Peterson, S. W.; Candela, G. A.; Swartzendruber, L. J.; Miller, J. S., "Crystal and Molecular Structure of the Paramagnetic 1:1 Decamethylferro-

- cenium 7,7,8,8-Tetracyano-*p*-quinodimethanide Dimer Salt: $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+ (\text{TCNQ})_2^{2-}$," *J. Am. Chem. Soc.* **1979**, *101*, 2756.
- (b) Miller, J. S.; Reis, A. H., Jr.; Gebert, E.; Ritsko, J. J.; Salaneck, W. R.; Kovnat, L.; Cape, T. W.; Van Duyne, R. P., "Synthesis and Characterization of Metamagnetic 1:1 1-D Phase of the Decamethylferrocenium 7,7,8,8-Tetracyano-*p*-quinodimethanide: $\text{Fe}[\text{C}_5(\text{CH}_3)_5]_2^+ [\text{TCNQ}]^-$," *J. Am. Chem. Soc.* **1979**, *101*, 7111.
- (c) Ward, M. D.; Johnson, D. C., "Electrocrystallization and Structural and Physical Properties of Charge-Transfer Complexes Derived from $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{M}]^{2+}$ (M = Fe, Ru) and TCNQ (TCNQ = Tetracyanoquinodimethane)," *Inorg. Chem.* **1987**, *26*, 4213.
- (d) Miller, J. S.; Zhang, J. H.; Reiff, W. M.; Dixon, D. A.; Preston, L. D.; Reis, A. H., Jr.; Gebert, E.; Exitine, M.; Troup, J.; Epstein, A. J.; Ward, M. D., "Characterization of the Charge-Transfer Reaction Between Decamethylferrocene and 7,7,8,8-Tetracyano-*p*-quinodimethane (1:1). The ^{57}Fe Mössbauer Spectra and Structure of the Paramagnetic Dimeric and the Metamagnetic One-Dimensional Salts and the Molecular and Electronic Structures of $[\text{TCNQ}]^n$ (n = 0, -1, -2)," *J. Phys. Chem.* **1987**, *91*, 4344.
8. (a) Ward, M. D., "Linear Chain Organometallic Donor-Acceptor Complexes and One-Dimensional Alloys. Synthesis and Structure of $[(\eta^6\text{-C}_6\text{Me}_3\text{H}_3)_2\text{M}][\text{C}_6(\text{CN})_6]$ (M = Fe, Ru)," *Organometallics* **1987**, *6*, 754.
- (b) Ward, M. D., "Electrochemical Aspects of Low-Dimensional Molecular Solids," *Electroanal. Chem.* **1988**, *16*, 181.
- (c) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. "Molecular Engineering of Solid-State Materials: Organometallic Building Blocks," *J. Am. Chem. Soc.* **1989**, *111*, 1698.
- (d) Ward, M. D.; Fagan, P. J.; Calabrese, J. C.; Johnson, D. C., "Electrostatic Structural Enforcement in Low-Dimensional Solids: Synthesis, Structure, and Electronic Properties of Polycationic Ruthenium Complexes," *J. Am. Chem. Soc.* **1989**, *111*, 1719.