Electronic Supplementary Information Available for

Quantitative Structure Analysis of the Unusual Long-Distance Bonding in Delocalized π-Dimer of Tetracyanopyrazine Ion-Radical

Sergiy V. Rosokha,* Jianjiang Lu, Bing Han and Jay K. Kochi

Department of Chemistry, University of Houston, Houston TX 77204,

Unit cell of the tetracyanopyrazine (**TCP)** crystal (Figure S1); electronic spectrum of $\mathbf{TCP}^{-\bullet}$ anion-radical (Figure S2); structures of **TCP** complexes with tetrathiafulvalene, biphenylene and pyrene (Figure S3); ion-radical π-associations via the bonding combination of their SOMOs for **TCNE,** naphthalene and p-chloranyl radicals (Figure S4); SOMO of ion radicals and HOMO of π-dimer for **TCNE**, p-chloranyl and **TCP** anion-radicals (Figure S5); HOMO, LUMO and LUMO+1 of **TCP** (Figure S6); HOMO of $(\mathbf{TCP})_2^{2-}$ dimer drawn with different boundary density conditions (Figure S7), molecular structure of sigma-bonded dimer σ-$(\mathbf{TCP})_2^{2-}$ salt with $[K^+$(cryptand)] counter-ion (Figure S8), complete reference 30, structural comparison of monomeric and π-bonded ion-radical of **DDQ,** p-chloranyl and ocrtamethylanthracene (Table S1).

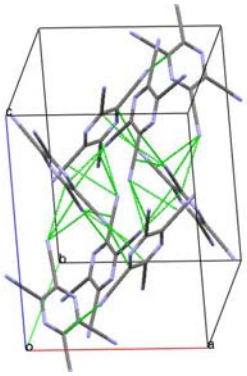


Figure S1. Unit cell of the crystal of **TCP** with green lines identifing the short intermolecular contacts.

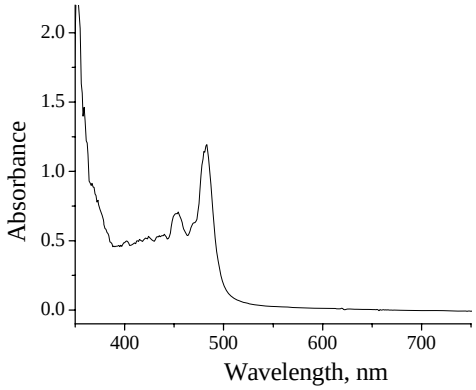


Figure S2. Electronic spectrum of **TCP**$^{-\bullet}$ anion-radical (0.5 mM solution in tetrahydrofuran measured with HP-845 UV-Vis spectrophotometer in 4-mm quartz cuvette).

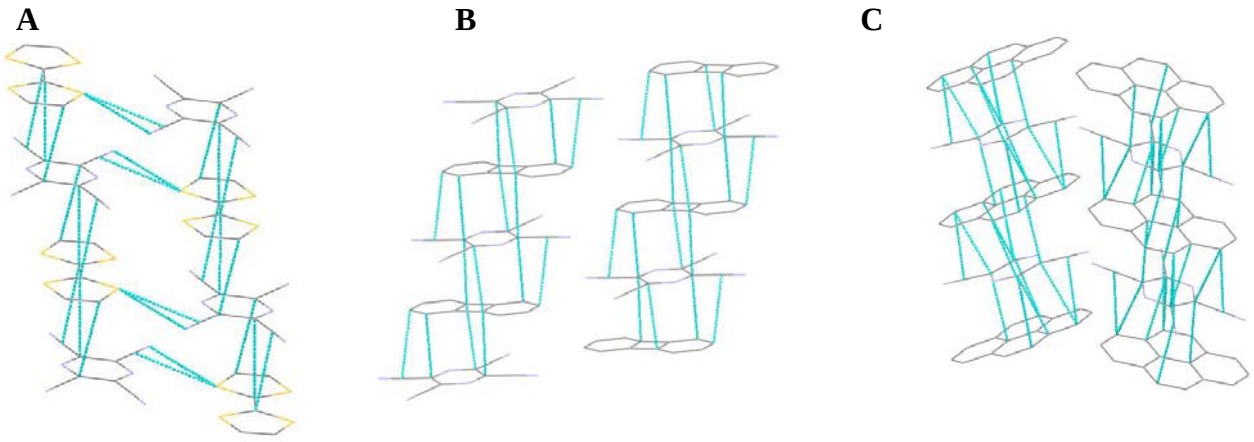


Figure S3. Alternating donor/acceptor stacks in the charge-transfer complexes of tetracyano-pyrazine acceptor with A) tetrathiafulvalene, B) biphenylene and C) pyrene donors. (The blue lines represent interatomic contact that are shorter than the van der Waals separations).

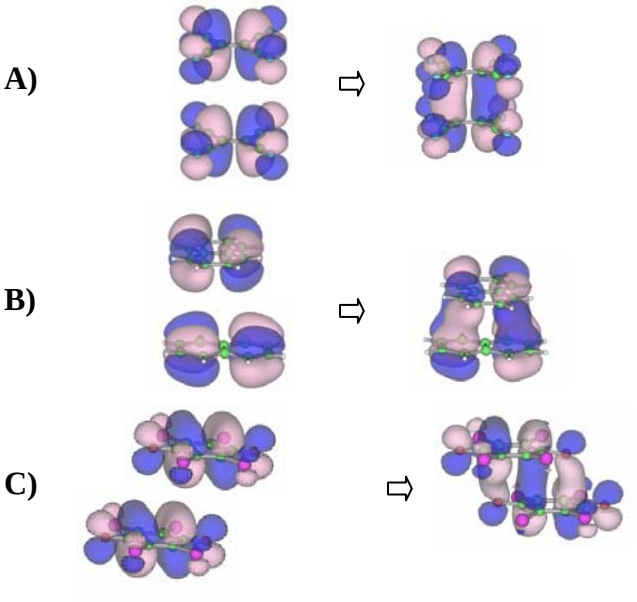


Figure S4. Illustrations of ion-radical π-associations via the bonding combination of their SOMOs: A) fully-eclipsed dimer of TCNE anion radical, B) laterally shifted dimer of *p*-chloranil anion-radicals, C) crossed associate of naphthalene cation-radicals.

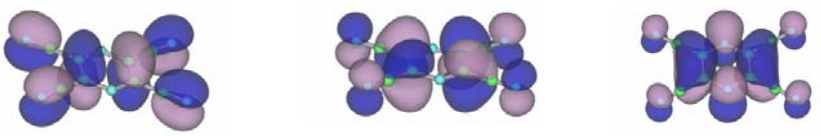


Figure S5. Frontier orbirals of tetracyanopyrazine acceptor.

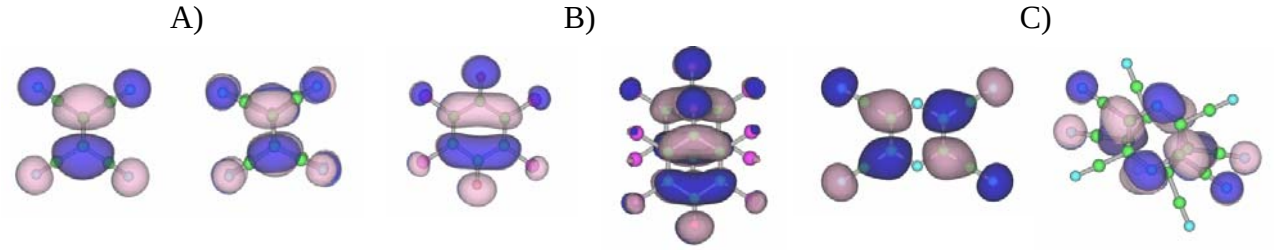


Figure S6. Comparison of the SOMO of ion radicals and HOMO of π-dimer demonstrating similarities of the corresponding orbitals in for the tetracyanoethylene (A) and p-chloranil (B) anion-radicals in contrast to the distinctively different orbitals of monomeric and dimeric tetracyanopyrazine species (C).

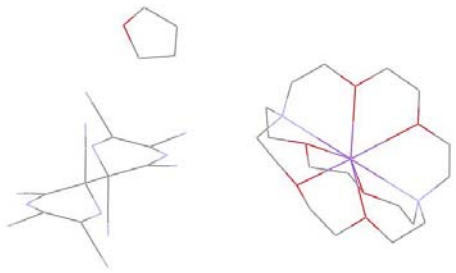
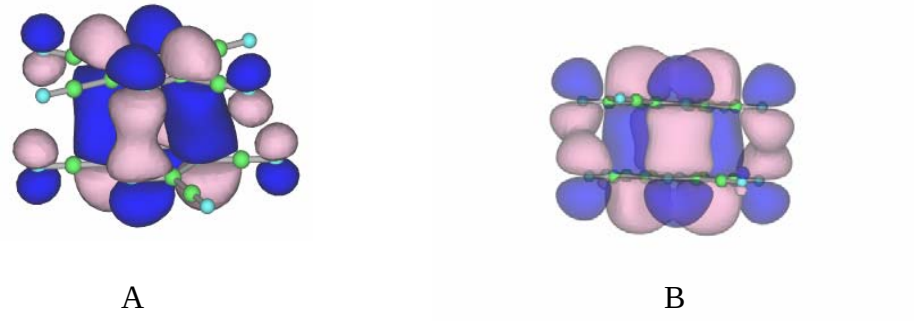


Figure S7. Molecular structure of the σ-dimer of the tetracyanopyrazine in its salt with [K^+(cryptand)] counter-ion.

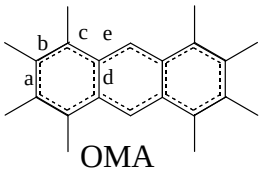


A B

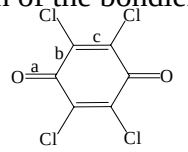
Figure S8. Molecular orbital (HOMO) of the $(\mathbf{TCP})_2^{2-}$ dimer visualized with different isosurface function value au(-3/2) of 0.02 (A) and 0.005 (B) showing additional bonding overlap between two pairs of terminus nitrogens at lower boundary density value.

COMPLETE REFERENCE 29. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J. A. Montgomery, J.; R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi; B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala,Q. Cui, K. Morokuma, P. Salvador, J.J. Dannenberg, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul,; B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P.M. W. Gill, B. Johnson, W. Chen, M.W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J.A. Pople, Gaussian 98; Revision A.11.3 ed.; Gaussian, Inc.: Pittsburgh, PA, 2001.

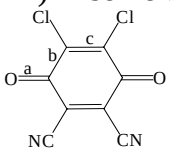
Table S1. Comparison of the bondlength Å) in some dimeric and monomeric ion-radicals.



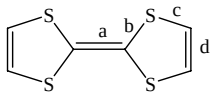
OMA



CA



DDQ



TTF

Ion-radical	Type	a	b	c	d	e	CCDC REFCODE
$OMA^{+\bullet}$	monomer	1.412 1.412	1.399 1.396 1.396 1.399	1.429 1.431 1.431 1.429	1.422 1.422	1.409 1.416 1.416 1.409	SONXUO
	dimer	1.422 1.424	1.408 1.400 1.394 1.397	1.425 1.426 1.425 1.419	1.443 1.434	1.399 1.401 1.406 1.398	SONXUO01
$CA^{-\bullet}$	monomer	1.249 1.247	1.446 1.444 1.452 1.449	1.358 1.362			WEWMER
	dimer	1.249 1.252	1.454 1.454 1.456 1.453	1.362 1.366			IMEYAA
$DDQ^{-\bullet}$	monomer	1.247	1.454 1.444	1.369 1.384			MEFEQU
	dimer	1.244 1.247	1.471 1.437 1.452 1.456	1.363 1.385			BEKJUW
TTF	monomer	1.397	1.715 1.718	1.725 1.722	1.330		REQWIU
	dimer	1.408 1.399	1.707 1.707 1.711 1.721 1.704 1.721 1.708 1.724	1.709 1.710 1.731 1.725 1.728 1.744 1.731 1.721	1.308 1.305 1.290 1.320		ZZZBWA10