Supporting Information

A sulfur-rich π -electron acceptor derived from 5,5'-bithiazolidinylidene: charge-transfer complex vs. charge-transfer salt

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Figure S1. ORTEP drawing of **4** with the numbering scheme. Thermal ellipsoids drawn at 50 % probability level.



Figure S2. ORTEP drawing of the acceptor 1 with the numbering scheme. Thermal ellipsoids drawn at 50 % probability level.



Figure S3. ORTEP drawing of **1** and TMTTF in [TMTTF][**1**] with the numbering scheme. Thermal ellipsoids drawn at 50 % probability level.



Figure S4. ORTEP drawing of 1^{-•} and [Fe(Cp*)₂]⁺ in [Fe(Cp*)₂][1] with the numbering scheme. Thermal ellipsoids drawn at 50 % probability level.

Computational Details

Full geometry optimization of DEBTTT, **1**, **1**- and TCNQ with Density Functional Theory¹ calculations were performed with the hybrid Becke-3 parameter exchange functional $(B3LYP)^2$ and the Lee-Yang-Parr nonlocal correlation functional³ implemented in the *Gaussian 09* (revision D.01) program suite.⁴ The 6-311G** basis set⁵ was used. The figures were generated with Gaussview 4.3.⁶ DEBTTT optimized coordinates are available in reference 7.

[1] (a) Hohenberg, P. Kohn, W. *Phys. Rev.* **1964**, *136*, B864. (b) R. G. Parr, W. Yang, *Density-Functional Theory of Atoms and Molecules*; Oxford University Press 1989.

[2] (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

[3] Lee, C.; Yang, W.; Parr, R. G. Phys. ReV. B 1988, 37, 785.

[4] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

[5] (a) McLean, A. D.; Chandler, G. S. *J Chem Phys* **1980**, *72*, 5639. (b) Wachters, A. J. H. *J Chem Phys* **1970**, *52*, 1033. (c) Hay, P. J. *J Chem Phys* **1977**, *66*, 4377. (d) McGrath, M. P.; Radom, L. *J Chem Phys* **1991**, *94*, 511.

[6] GaussView, Version 5.0.9, Roy Dennington, Todd Keith, and John Millam, *Semichem Inc.*, Shawnee Mission, KS, 2009.

[7] Y. Le Gal, N. Bellec, F. Barrière, R. Clérac, M. Fourmigué, V. Dorcet, T. Roisnel, D. Lorcy *Dalton Transactions*, **2013**, *42*, 16672-16675.

1 optimized geometry coordinates



HF = -2537.2231181 hartrees (File name accCN)	
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charge 0 multiplicity 1						
S	5.48951300	4.24213600	2.34614600			
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Ν	3.63539300	2.34669200	2.79920300			
С	4.01448500	2.32600100	4.23367500			
С	3.19098800	3.29712500	5.07591100			
С	2.64415000	1.57266400	2.25999400			
С	1.80927000	0.65699600	2.87347700			
С	0.85785300	-0.03474500	2.06789300			
Ν	0.08675100	-0.59399300	1.41183800			
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Ν	1.71940800	0.02934800	5.37119400			
S	2.46178000	2.53719000	-2.34578600			
S	5.48626000	4.93633600	-0.51414300			
С	4.19684300	3.73422200	-0.55362600			
С	3.67234600	3.58181000	-1.90713300			
Ν	4.31584200	4.43265100	-2.79914500			
С	3.93662900	4.45328100	-4.23358600			
С	4.76003200	3.48209900	-5.07584600			
С	5.30711000	5.20672200	-2.26004600			
С	6.14192800	6.12237300	-2.87363800			
С	7.09337600	6.81419000	-2.06815600			
Ν	7.86449600	7.37351400	-1.41218600			
С	6.16592300	6.45077800	-4.25565900			
Ν	6.23159400	6.74990800	-5.37139000			
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Н	3.33572800	4.32555500	4.74142700			
Н	3.51754900	3.22631600	6.11575800			
Н	2.12733000	3.05715400	5.04556700			
Н	2.88106100	4.18883200	-4.26300300			
Н	4.03731900	5.47627700	-4.58573400			
Н	4.61524400	2.45368100	-4.74134500			
Н	4.43343600	3.55292200	-6.11568100			
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<u>1</u>. optimized geometry coordinates



\HF= -2537.354108 hartrees\ (File name accCN1m)

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4.32300000	3.17000000	1.88100000				
3.68100000	2.32900000	2.77600000				
4.02700000	2.35200000	4.21300000				
3.11100000	3.27700000	4.98500000				
2.67700000	1.58400000	2.23600000				
1.84300000	0.68200000	2.86900000				
0.78400000	0.08100000	2.12300000				
-0.08800000	-0.40000000	1.58100000				
1.91500000	0.26900000	4.23000000				
1.90700000	-0.12600000	5.29900000				
2.39500000	2.59900000	-2.26700000				
5.48300000	4.91700000	-0.51300000				
4.19300000	3.74300000	-0.54600000				
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3.92400000	4.42800000	-4.21300000				
4.84000000	3.50200000	-4.98500000				
5.27400000	5.19600000	-2.23600000				
6.10800000	6.09800000	-2.86900000				
7.16700000	6.69800000	-2.12300000				
8.03900000	7.17900000	-1.58100000				
6.03600000	6.51100000	-4.23000000				
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3.95800000	1.45500000	4.57500000				
3.14400000	4.15500000	4.59900000				
3.39600000	3.31800000	5.90000000				
2.21200000	2.94300000	4.94500000				
3.00700000	4.13200000	-4.31700000				
3.99400000	5.32500000	-4.57500000				
4.80700000	2.62400000	-4.59900000				
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4.55500000

5.73900000

3.46100000 -5.90000000

3.83600000 -4.94500000

Η

Η

6

TCNQ optimized geometry coordinates



HF= - hartrees (File name TCNQ)

charge 0 multiplicity 1

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Ν	-0.25900200	-0.14730700	-1.11425300
С	-2.70006900	-0.94947700	-3.42943900
Ν	-3.62671500	-1.63642400	-3.50839500
С	0.02843600	3.18050000	-7.61690400
С	1.16857100	4.02856400	-7.52916200
Ν	2.09559200	4.71504300	-7.45057000
С	-0.68665400	3.20815800	-8.84768700
Ν	-1.27235700	3.22576800	-9.84440900
С	-1.90648400	0.72659200	-5.63879600
С	-1.16925600	0.70899100	-4.39529500
С	-0.00940400	1.56545500	-4.28977000
С	0.37300400	2.35508600	-5.31848900
С	-0.36376000	2.37212400	-6.56226100
С	-1.52404200	1.51619600	-6.66751300
Н	-2.77886000	0.09209000	-5.73622000
Η	0.55505700	1.56581100	-3.36540700
Η	1.24504500	2.99000200	-5.22081300
Н	-2.08877300	1.51616500	-7.59171000