Supporting Information

Diversity and uniformity in anion-π complexes of thiocyanate with aromatic, olefinic and quinoidal π-acceptors.

Joshua Wilson,[†] Tristan Maxson,[†] Isabelle Wright,[†] Matthias Zeller,[‡] and Sergiy V. Rosokha*,[†]

[†]Department of Chemistry, Ball State University, Muncie, Indiana, 47306, United States

[‡]Department of Chemistry, Purdue University, West Lafayette, Indiana, 47907, United States

E-mail: svrosokha@bsu.edu

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Calculation of the equilibria constants

Formation constants of the complexes, [A, NCS^-], between thiocynate and various π-acceptors were established via UV-Vis measurements of the acetonitrile or dichloromethane solutions (at 22 °C) containing constant concentrations (from 1 to 10 mM) of A and variable concentrations (from 0 to ~ 0.4M) of tetrapropylammonium or tetrabutylammonium salts of thiocyanate (the measurements with Bu_4NNCS or Pr_4NNCS salts afforded the same within the accuracy limits results). The formation constants and spectral characteristics represent average values from 3-5 series of UV-Vis experiments for each A/NCS^- pair. Each such series typically included 8 -10 points.

The measurements were carried out in capped quartz (1.0 mm or 1.0 cm path length) spectroscopic cuvettes equipped with a sidearm under argon atmosphere. To avoid interference from the irreversible (time-dependent) reactions which were observed in the solutions containing thiocyanate and pFA, TCNE, or TCP, the measurements with these acceptors were carried out immediately after mixing (typically within 10 s) on a HP 8453 diode-array spectrometer (the spectra of the solutions did not show any sign of the side products on this time scale). With the DDQ, pCA, pBA, oCA acceptors, the formation of byproduct was noticeable immediately after mixing of reagents at room temperature. Complex formation with these acceptors was observed in dichloromethane solutions at low temperatures. These measurements were carried out on a CARY 500 spectrophotometer using a Dewar equipped with quartz lens. The temperature in the Dewar (from +5 to -90 °C) was adjusted with an ethanol-liquid nitrogen bath (±0.5 K).

Extinction coefficients ε for [A,NCS^-] complexes and equilibrium constants of their formation, K were calculated via regression analysis of the dependence of the differential intensity of absorption (obtained by subtraction of absorption of components from the absorption of their mixtures) of solutions containing constant concentrations of A and variable concentrations of thiocyanate salt:

$$A + NCS^- \overset{K}{\rightleftharpoons} [A, NCS^-] \qquad (S1)$$

The formation constant of the complex is expressed as

$$K = C_{com} / ((C^o_D - C_{com})(C^o_A - C_{com})) \qquad (S2)$$

where C_{com} is the concentartion of the complex, and C^o_D and C^o_A are initial concentrations of NCS^- and A, respectively. From eq. S2, concentration of complex is expressed as:

$$C_{com} = (C^o_A + C^o_D + 1/K_{eff}) +/- (((C^o_A + C^o_D + 1/K_{eff})^2 - 4C^o_A C^o_D)^{0.5}\}/2 \qquad (S3)$$

So, changes in the UV-Vis absorption intensity can be expressed as:

$$\Delta Abs = \varepsilon l \times C_{com} = \varepsilon l \times \{(C^o_A + C^o_D + 1/K_{eff}) - ((C^o_A + C^o_D + 1/K_{eff})^2 - 4C^o_A C^o_D)^{0.5}\}/2 \qquad (S4)$$

where ε and l are extinction coefficient of the complex and the length of the cell. The fitting of the results of the UV-Vis titrations to eqs S4 (with ε and K as the ajustable parameters) using the Origin Pro 2016 is illustrated in Figures S1 – S5. Such fits produced values of K and ε in Table 1.

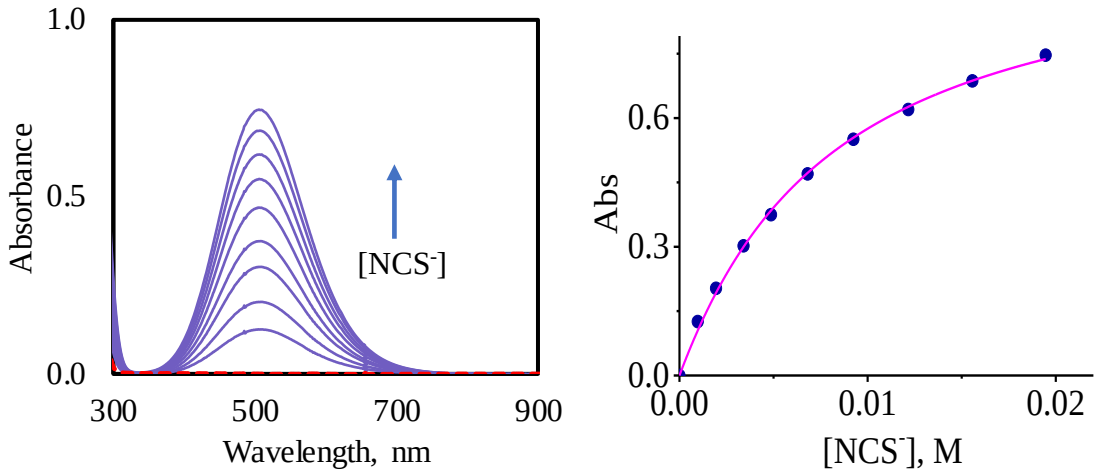


Figure S1. (Left) Spectra of solutions with constant concentration of TCNE (1.6 mM) and variable concentration of $(Bu_4N)NCS$ (in CH_2Cl_2, at 22 °C). Spectrum of an individual TCNE is shown as a dashed red line. (Right) The fit of absorption intensities at λ=506 nm using a 1:1 TCNE/NCS^- binding model.

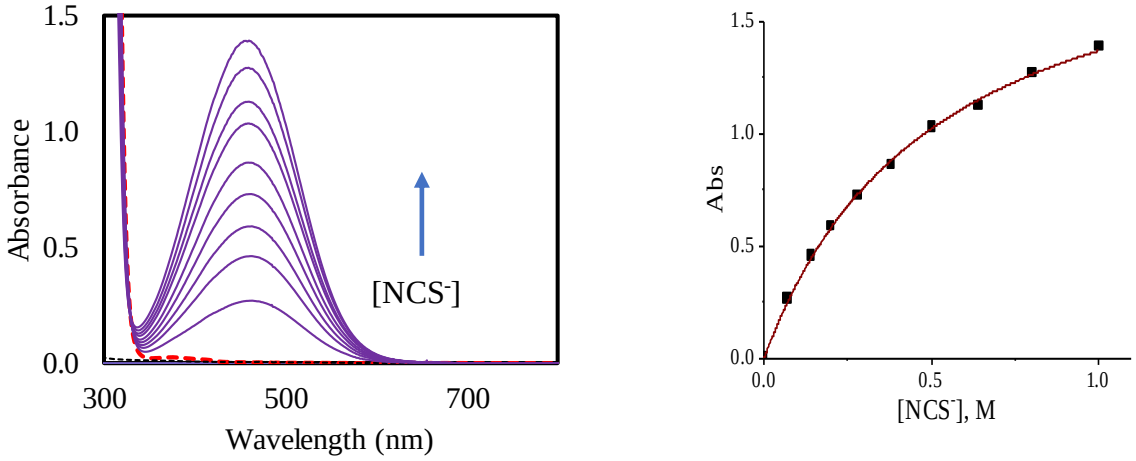


Figure S2. (Left) Spectra of solutions with constant concentration of TCP (6.3 mM) and variable concentration of $(Bu_4N)NCS$ (in CH_3CN, at 22 °C). Spectrum of an individual TCP and $(Bu_4N)NCS$ are shown as dashed red and black lines, respectively. (Right) The fit of absorption intensities at λ=461 nm using a 1:1 binding model.

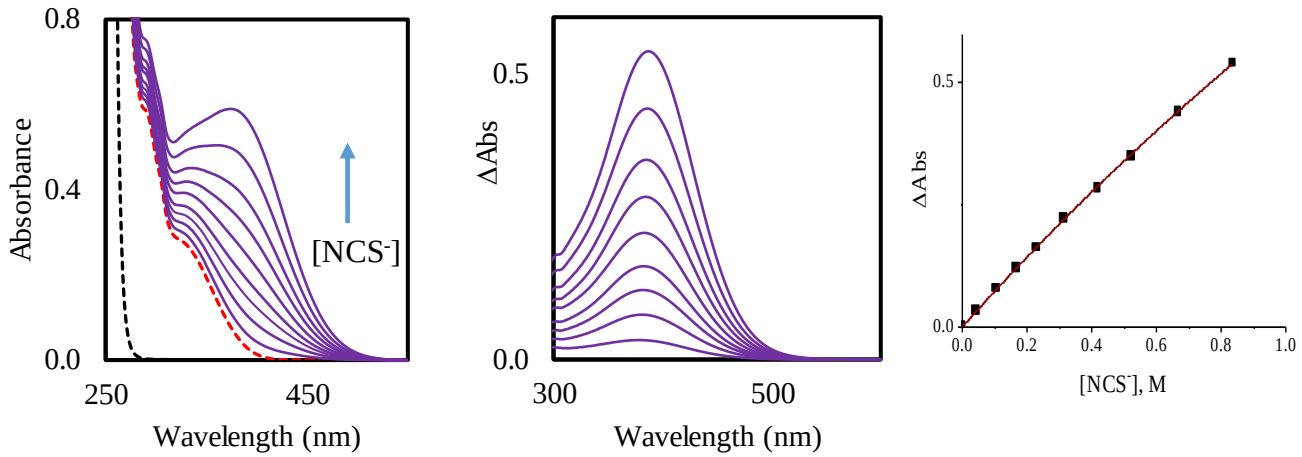


Figure S3. (Left) Spectra of solutions with constant concentration of TNB (13 mM) and variable concentration of $(Bu_4N)NCS$ (in CH_3CN, at 22 °C) Black and red dashed line show spectra of individual $(Bu_4N)NCS$ and TNB. (Middle) Spectra of the same solutions after subtraction of absorption of components. (Right) The fit of absorption intensities at λ=386 nm using a 1:1 binding model.

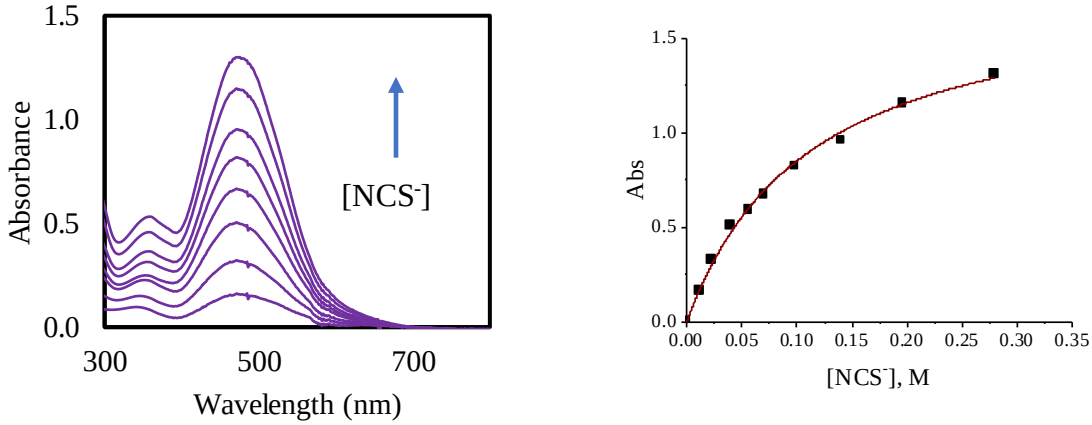


Figure S4. (Left) Spectra of solutions with constant concentration of pFA (4.3 mM) and variable concentration of $(Bu_4N)NCS$ (in CH_2Cl_2, at 22 °C). (Right) The fit of absorption intensities at λ=472 nm using a 1:1 binding model.

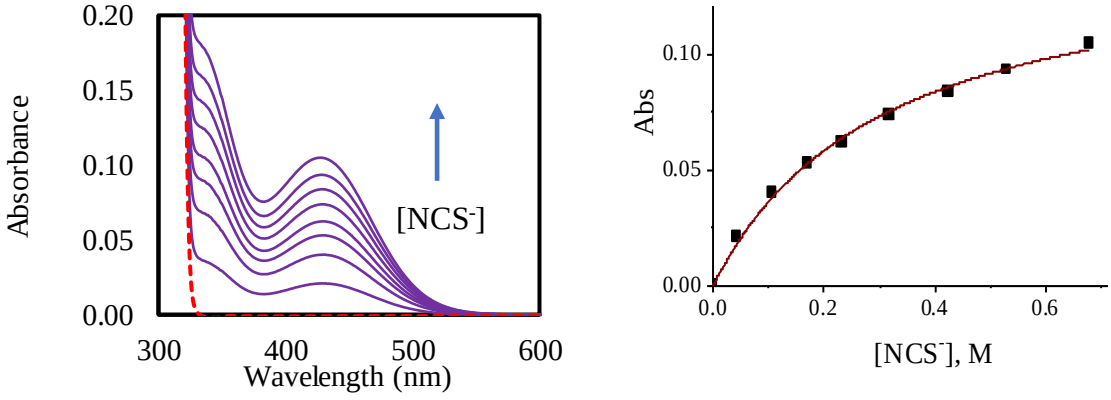


Figure S5. (Left) Spectra of solutions with constant concentration of TCB (2.5 mM) and variable concentration of $(Bu_4N)NCS$ (in CH_2Cl_2, at 22 °C). (Right) The fit of absorption intensities at λ=428 nm using a 1:1 binding model.

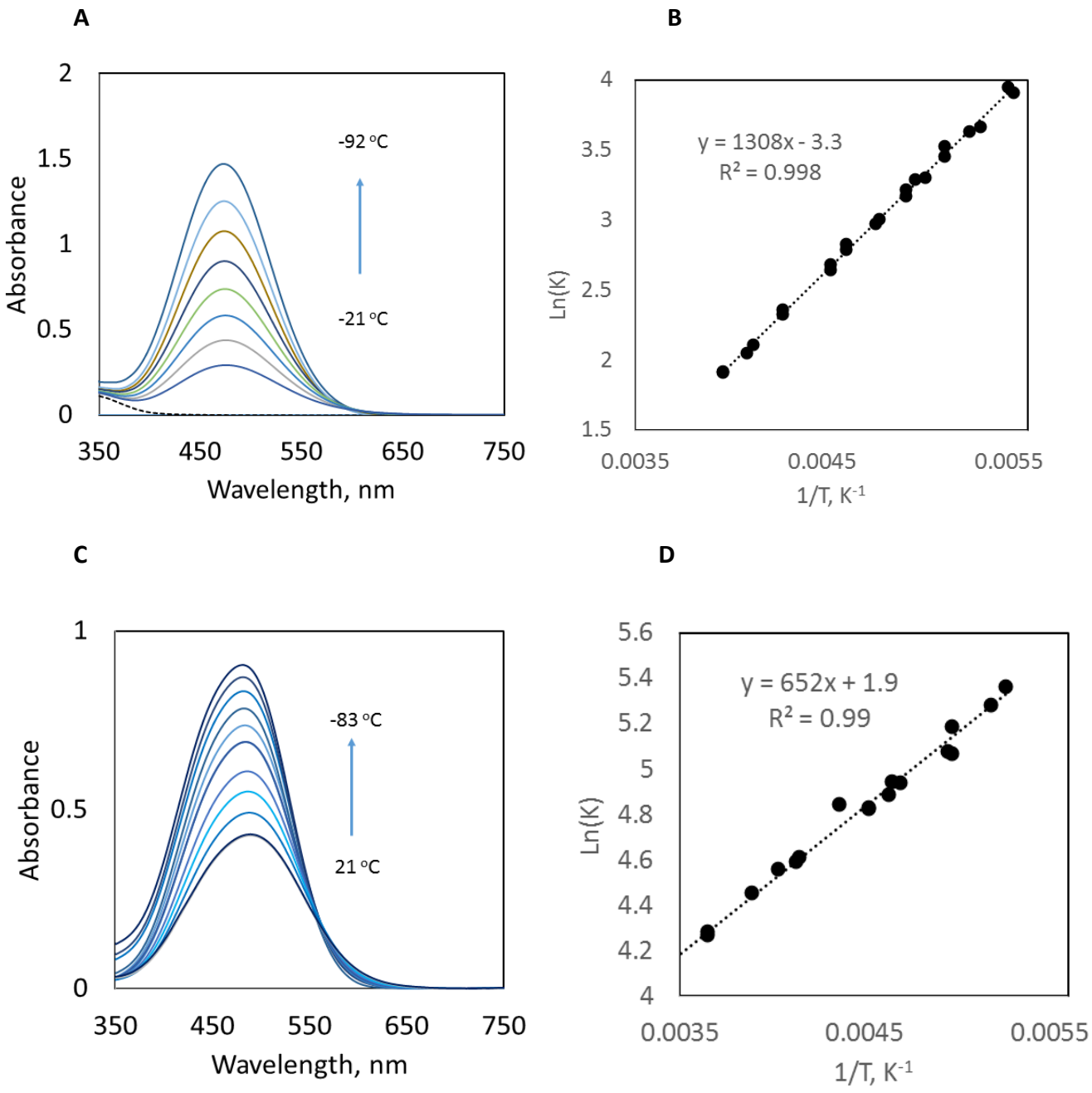
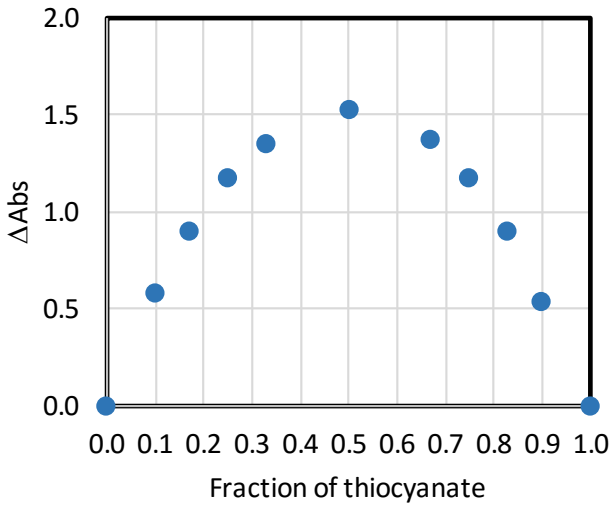
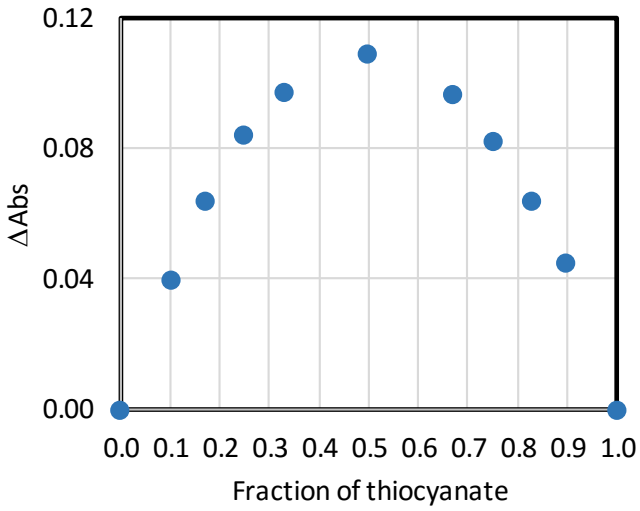


Figure S6. Temperature dependence of the UV-Vis spectra for the solutions containing mixtures of $(Bu_4N)NCS$ and pFA (A) or TCP (C) in dichloromethane and the corresponding van't Hoff plots of the temperature dependence of formation constants for the anion-π complexes [pFA, NCS^-] (B) and [TCP, NCS^-] (D). Concentration of reactants: 0.59 mM pFA and 11 mM $(Bu_4N)NCS$ (A, B) and 0.65 mM TCP and 6.1 mM $(Bu_4N)NCS$ (C,D).

A



B



C

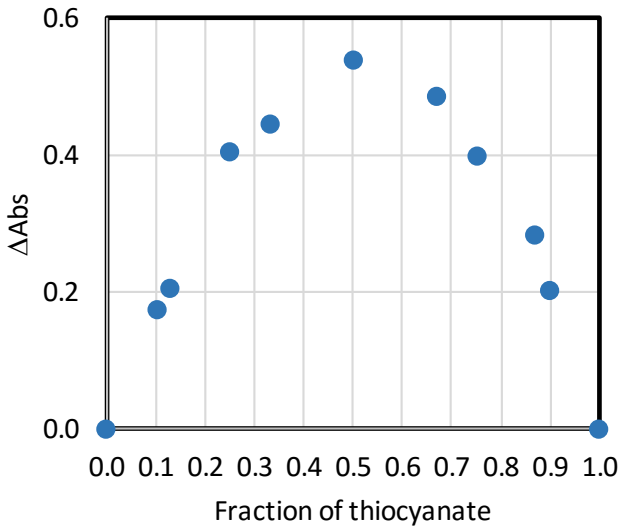


Figure S7. Jobs plots: dependencies of ΔAbs on the molar fraction of thiocyanate in the acetonitrile solutions containing π-acceptors A and Bu_4NNCS with the constant sum of concentration of components. A) A = TCNE, sum of concentrations of components: 28 mM. B) A = TCP, sum of concentrations of components: 20 mM. C) A = pFA, sum of concentrations of components: 35 mM.

Table S1. Energies of the (lowest-energy) absorption bands of the complexes of halide anions with different acceptors (for Mulliken correlation in Figure 2).

Acceptor, A	E_{red} (A),[a, b] V vs SCE	hν, eV [A,Br^-][a]	[A,I^-][a]	[A,Cl^-][a]	[A,NCS^-]
DDQ	0.52	2.182		2.820	2.409
TCNE	0.17	2.668			2.481
oCA	0.15	2.660			2.496
pBA	0.02	2.272	1.859	3.181	2.558
pFA	-0.01	2.833	2.103	3.223	2.634
pCA	-0.02	2.733	2.001	3.094	
$26Cl_2Q$	-0.18	2.885	2.195	3.300	
$25Cl_2Q$	-0.20	2.885	2.204	3.317	
TCP	-0.22	3.102	2.256	3.446	2.691
TNB	-0.42	3.446	2.697		3.181
TCB	-0.65	3.495	2.532		2.990

a) From: Kepler, S.; Zeller, M.; Rosokha, S.V. Anion–π complexes of halides with p-benzoquinones: structures, thermodynamics, and criteria of charge transfer to electron transfer transition *J. Am. Chem. Soc.*, **2019**, 141, 9338 – 9348. b) E_{ox} for I^-, Br^-, Cl^- and NCS^- are 1.06, 1.60, 2.03 and 1.52 V vs SCE, respectively. The value for I^-, Br^-, Cl^- are from and the value for NCS^- was calculated as described in: Isse, A.A.; Lin, C. Y.; Coote, M. L.; Gennaro, A. Estimation of standard reduction potentials of halogen atoms and alkyl halides. *J. Phys. Chem. B*, **2011**, 115, 678-684.

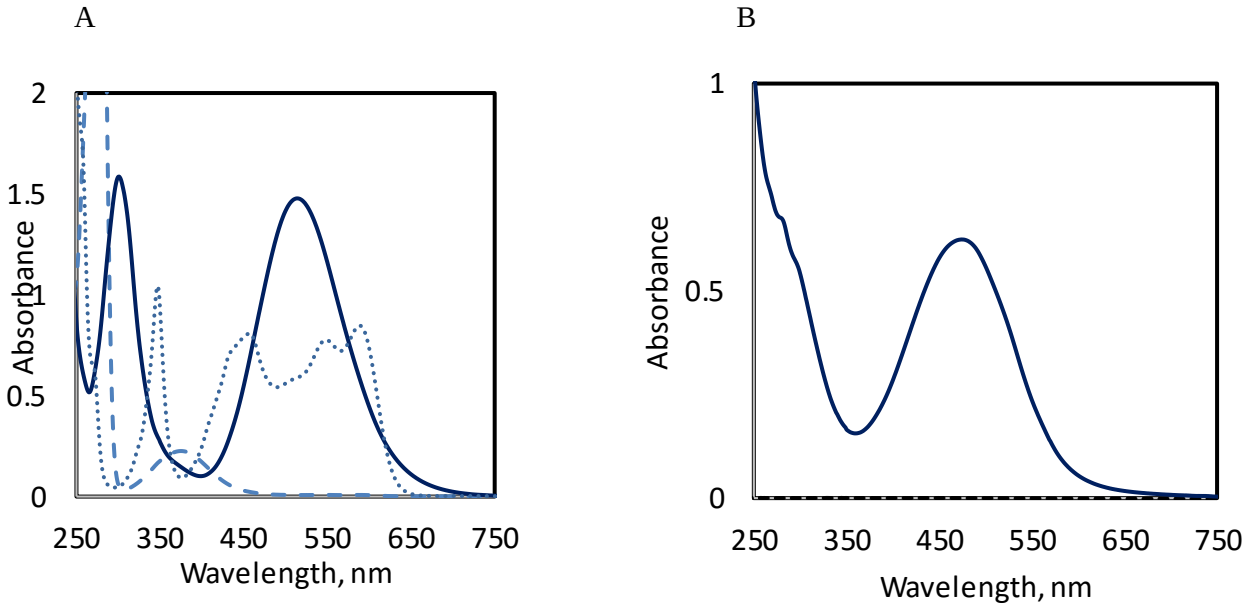


Figure S8. Low-temperature (-80 C) UV-Vis spectra of the solutions containing $(Bu_4N)NCS$ and DDQ (A) or oCA (B) in dichloromethane showing spectra of the [DDQ, NCS^-] and [oCA, NCS^-] complexes as solid dark blue lines. Spectra of the neutral DDQ acceptors (dashed line) and $DDQ^{-\bullet}$ anion-radical (dotted line) are shown in A for comparison.

Details of preparation of single crystals and X-ray structural analysis

Table S2. Crystallographic, data collection, and structure refinement details.

	pFA•NCS$^-$	TCP•NCS$^-$	TCNE•NCS$^-$	TNB•NCS$^-$
Chemical formula	$1.5(C_6F_4O_2)\cdot C_{12}H_{28}N\cdot CNS$	$C_8N_6\cdot 2(C_{12}H_{28}N)\cdot 2(CNS)$	$C_6N_4\cdot 2(C_{12}H_{28}N)\cdot 2(CNS)$	$C_6H_3N_3O_6\cdot C_{12}H_{28}N\cdot CNS$
M_r	514.52	669.01	616.96	457.55
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$	Tetragonal, $I\bar{4}2d$	Orthorhombic, $P2_12_12_1$
Temperature (K)	150	150	150	150
a, b, c (Å)	10.2809 (17), 24.653 (4), 9.7480 (14)	9.6131 (11), 11.5468 (13), 17.891 (2)	14.7446 (7), 14.7446 (7), 34.4695 (18)	9.2223 (10), 12.5540 (16), 20.447 (3)
β (°)	90.110 (6)	90.086 (7)		
V (Å^3)	2470.7 (7)	1985.9 (4)	7493.8 (8)	2367.3 (5)
Z	4	2	8	4
Radiation type	Mo $K\alpha$	Cu $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.20	1.49	0.17	0.18
Crystal size (mm)	0.45 × 0.43 × 0.28	0.22 × 0.20 × 0.16	0.45 × 0.31 × 0.15	0.52 × 0.50 × 0.38
T_{min}, T_{max}	0.620, 0.746	0.369, 0.526	0.711, 0.747	0.669, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	28882, 7332, 5827	21437, 4230, 2898	45869, 7026, 5227	38913, 8366, 6968
R_{int}	0.059	0.096	0.036	0.038
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.725	0.643	0.770	0.769
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.045, 0.119, 1.05	0.062, 0.193, 1.05	0.043, 0.122, 1.04	0.036, 0.092, 1.05
No. of reflections	7332	4230	7026	8366
No. of parameters (restraints)	313	241(69)	222 (24)	313 (3)

Single crystals of anion-π complexes were obtained by diffusion of hexane into dichloromethane solutions containing p-benzoquinone and (Pr_4N)NCS salt at low temperatures (-75 °C) or by evaporation of equimolar solutions of TNB and the (Pr_4N)NCS salt in acetonitrile at 0 °C. For example, solutions of 49 mg of (Pr_4N)NCS (0.20 mmol) and 36 mg of F_4Q (0.20 mmol) in CH_2Cl_2 were mixed in a Schlenk tube at -78 °C. The resulting solution was layered with hexane. Slow diffusion of hexane into the dichloromethane (at -75 °C) resulted in the formation of red 1.5pFA• ((Pr_4N)NCS)·crystals. TCNE•2((Pr_4N)NCS) and TCP•2((Pr_4N)Br·F_4Q) crystals were prepared in a similar way.

Single crystals were analyzed using a Bruker AXS D8 Quest CMOS diffractometer with a Mo Kα wavelength sealed X-ray tube (pFA•NCS^-, TCNE•NCS^-, TNB•NCS^-) or a Bruker Quest CMOS diffractometer with a Cu Kα microsource X-ray tube (TCP•NCS^-). The Mo Kα wavelength Quest diffractometer is features a fixed chi angle, a sealed tube fine focus X-ray tube, single crystal curved graphite incident beam monochromator, a Photon100 CMOS area detector and an Oxford Cryosystems low temperature device. The Cu Kα instrument has a kappa geometry, an I-μ-S microsource X-ray tube, laterally graded multilayer (Goebel) mirror single crystal for monochromatization, a Photon-II CMOS area detector and also an Oxford Cryosystems low temperature device. Data were collected at 150 K, reflections were indexed and processed, and the files scaled and corrected for absorption using APEX2 [1].

For all compounds, the space groups were assigned and the structures were solved by direct methods using XPREP within the SHELXTL suite of programs [2] and refined by full matrix least squares against F^2 with all reflections using Shelxl2018 [3] using the graphical interface Shelxle [4]. If not specified otherwise H atoms attached to carbon atoms as well as hydroxyl hydrogens were positioned geometrically and constrained to ride on their parent atoms. C-H bond distances were constrained to 0.99 and 0.98 Å for aliphatic CH_2 and CH_3 moieties, respectively. Methyl CH_3 and oms were allowed to rotate but not to tip to best fit the experimental electron density. U_{iso}(H) values were set to a multiple of U_{eq}(C/O) with 1.5 for CH_3 and 1.2 for CH_2 units, respectively.

For pFA•NCS^- the structure is metrically orthorhombic but actually monoclinic and twinned by a 180 rotation around the a or c-axis. Application of the transformation matrix 1 0 0 , 0 -1 0, 0 0 -1 yielded a twin ratio of 0.561(1) to 0.439(1).

The structure of TCP•NCS^- emulates *P*nnm symmetry and is twinned by this symmetry. The higher Pnnm symmetry is mostly obeyed, but broken by partial ordering of the thiocyanate ion. In the *P*nnm setting, the anion is 1:1 disordered around a two-fold axis. In the actual $P2_1/n$ setting, the disorder is 0.685(5) to 0.315(5). Attempts to refine the structure in *P*nnm resulted in R values around 12%, double the value of $P2_1/n$. Splitting of reflections at high

angle is also observed. The structure was refined as a 2-component twin, twin transformation matrix 1 0 0, 0 -1 0, 0 0 -1. The Flack parameter refined to 0.505(3).
The two disordered thiocyanate moieties were restrained to have similar geometries. U^{ij} components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy ratio refined to 0.685(5) to 0.315(5).

In TCNE•NCS^- the isocyanate ions are 1:1 disordered around a two-fold axis (that coincides with a four-fold rotinversion axis). U^{ij} components of ADPs for disordered atoms closer to each other than 2.7 Å were restrained to be similar.

In TNB•NCS^- the isocyanate is disordered over two orientations. The occupancy ratio refined to 0.773(5) to 0.227(5).

Complete crystallographic data, in CIF format, have been deposited with the Cambridge Crystallographic Data Centre. CCDC 1984456 -1984459 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References.

[1] Bruker (2016). Apex3, Saint, Sadabs, Bruker AXS Inc.: Madison (WI), USA, 2018.

[2] a) SHELXTL suite of programs, Version 6.14, 2000-2003, Bruker Advanced X-ray Solutions, Bruker AXS Inc., Madison, Wisconsin: USA b) Sheldrick GM. A short history of SHELX. *Acta Crystallogr A*. **2008**, *64(1)*, 112–122.

[3] a) Sheldrick GM. University of Göttingen, Germany, **2018**. b) Sheldrick GM. Crystal structure refinement with SHELXL. *Acta Crystallogr Sect C Struct Chem*. **2015**, *71(1)*, 3–8.

[4] Hübschle CB, Sheldrick GM, Dittrich B. ShelXle: a Qt graphical user interface for SHELXL. *J. Appl. Crystallogr*. **2011**, *44(6)*, 1281–1284.

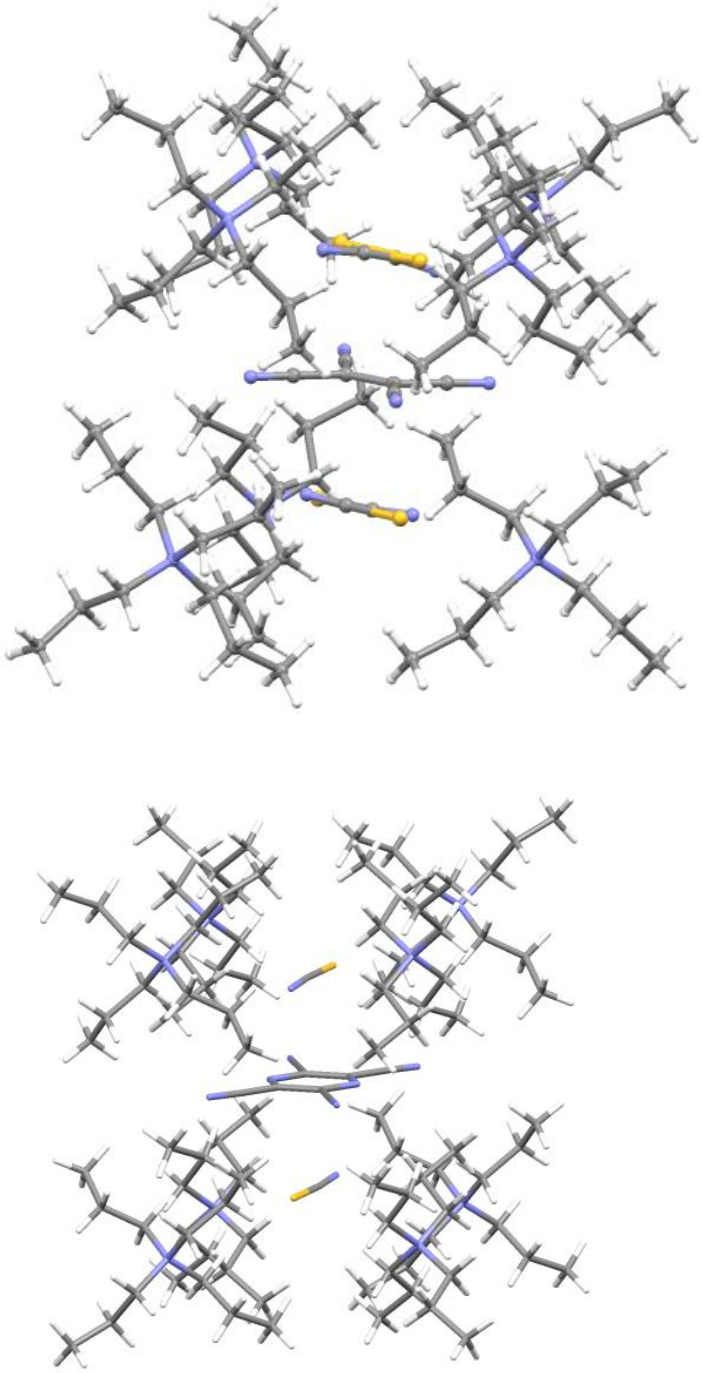


Figure S9. Fragments of the X-ray structures of TCNE•2((Pr_4N)NCS) (top) and TCP•2((Pr_4N)NCS) showing discrete 2:1 ($2NCS^-$:A) complexes surrounded by counter-ions.

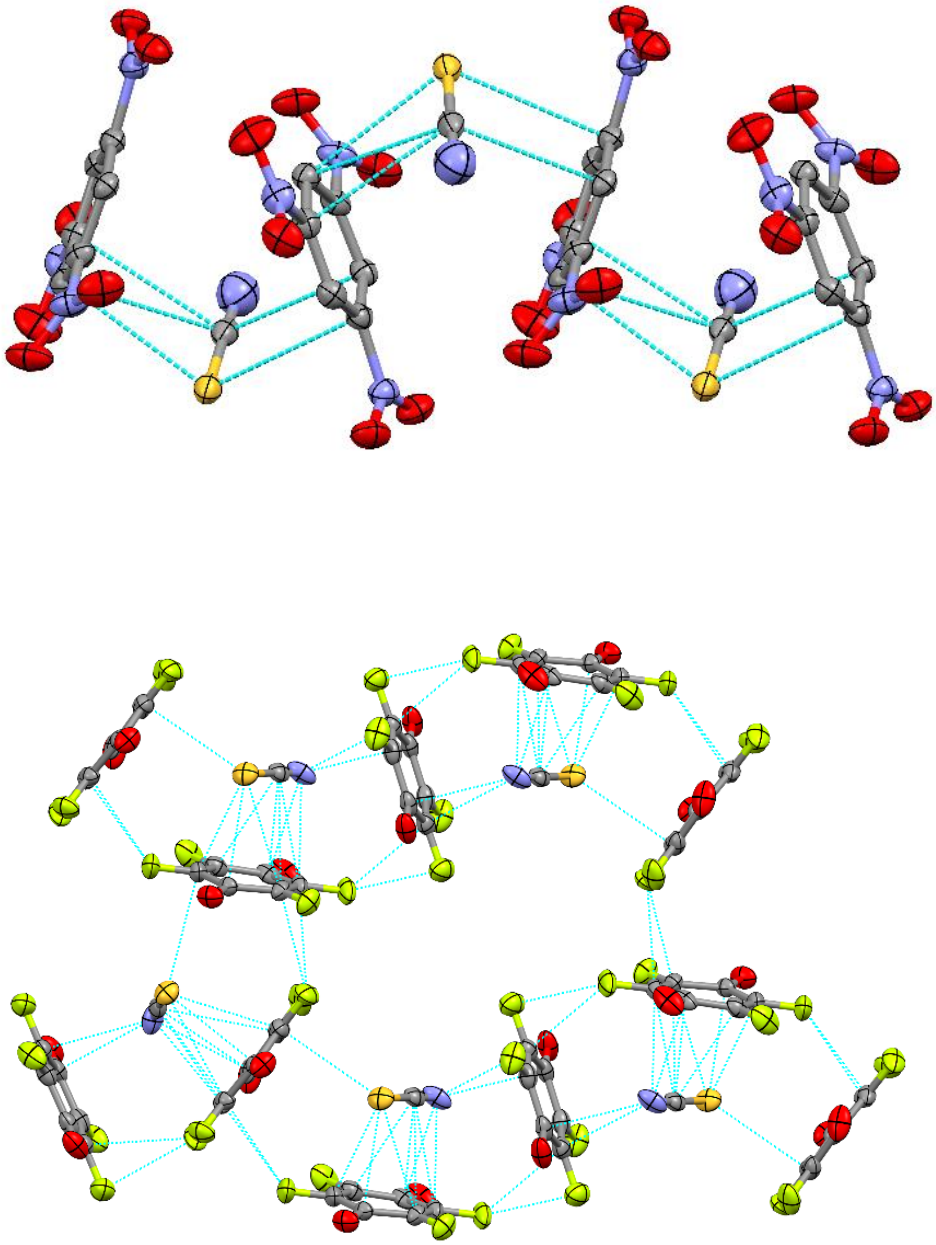


Figure S10. Alternating donor/acceptor chains formed by anion-π bonding between TNB molecules and thiocyanate anions (top) and quazi-2D layers formed by pFA molecules and thiocyanate anions (bottom).

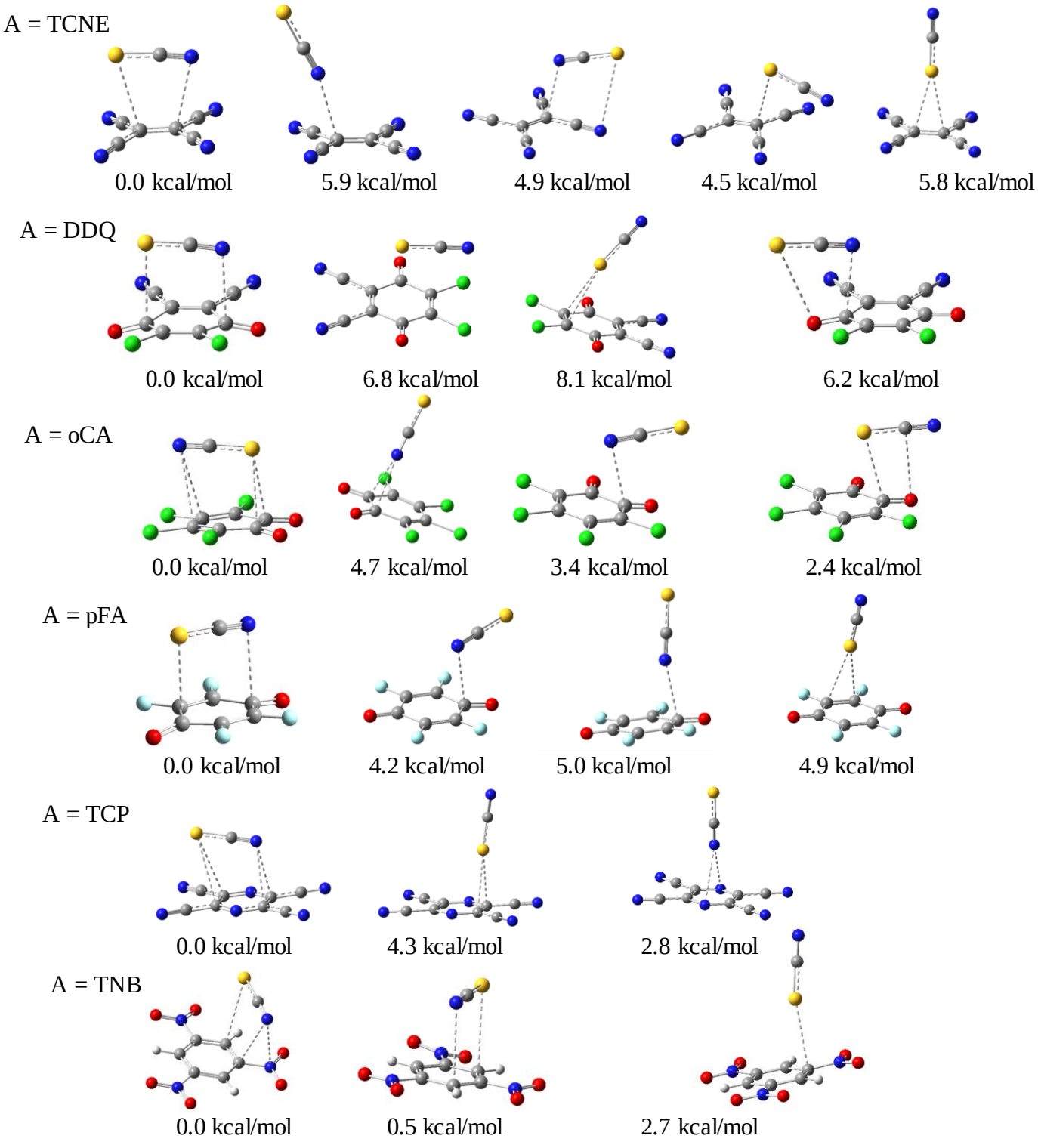


Figure S11. Energies of the local-minima structures for the A•NCS^- dyads (as indicated) relative to that of the most stable structure (from M062X/def2tzvpp computations in CH_3CN).

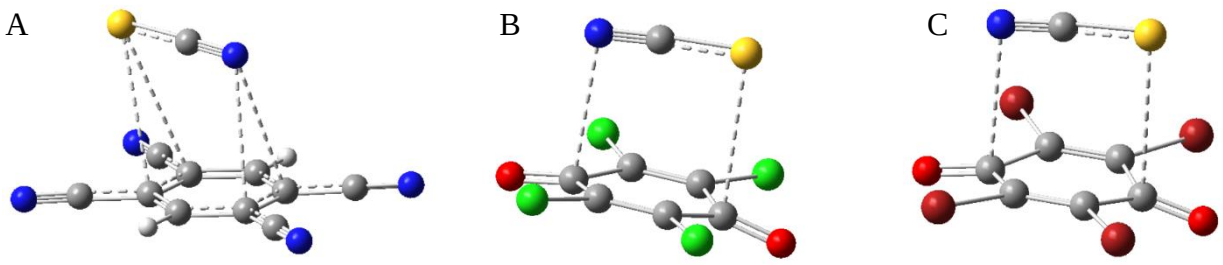


Figure S12. Optimized structures of the complexes of thiocyanate with TCB (A), pCA (B) and pBA (C) (from M062X/def2tzvpp computations in CH_3CN).

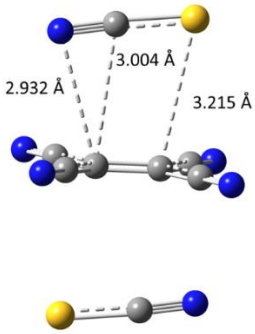


Figure S13. Structure of the calculated 2:1 complex (M062X/def2tzvpp computations in CH_3CN).

Table S3. Calculated characteristics of the [A,NCS] complexes (M062X/def2tzvpp computations in CH_3CN).[a]

A	ΔE,[b] kcal/mol	$d_{N\cdots C}$,[c] Å	$d_{S\cdots C}$, Å	λ, nm (log ε)	Δq,[d] e	Δq, e, (NBO)[e]	Δq, e, (NBO)[e]	V_{max}^{π}, a.u.
TCB	-4.47	3.169	3.053	432 (2.835)	0.042	0.026	0.030	0.065
TNB	-4.51	3.012	3.305	378 (3.598)	0.058	0.041	0.052	0.075
TCP	-6.99	2.997	3.367	463 (3.331)	0.067	0.080	0.047	0.107
pCA	-8.14	2.858	3.150	427 (3.764)	0.145	0.191	0.146	0.055
pFA	-7.75	2.852	3.117	414 (3.803)	0.141	0.168	0.131	0.070
pBA	-8.33	2.855	3.160	430 (3.750)	0.148	0.205	0.155	0.055
oCA	-9.51	3.140	3.014	421 (3.978)	0.197	0.184	0.203	0.067
TCNE	-8.98	2.855	3.052	448 (3.935)	0.201	0.267	0.220	0.081
DDQ	-12.15	2.799	3.022	444 (3.892)	0.248	0.306	0.263	0.089

a) From calculations with CH_3CN as a medium. b) $\Delta E = E_c - (E_{BQ} + E_X) + BSSE$, where E_c, E_{BQ} and E_X are sums of the electronic and ZPE of the optimized complex, BQ and anion and BSSE is a basis set superposition error, see Table S4 in the ESI for details. c) Shortest intermolecular N•••C distance, if not noted otherwise. d) From AIM analysis. e) From NBO analysis. f) From NBO analysis, calculations in CH_2Cl_2. F) Maximum electrostatic potential on the face of the individual π-acceptor (see Figure S 17) calculated at 0.001 a.u. electron density surface.

Table S4. Energies of the acceptors and [A,NCS^-] complexes (with def2tzvpp basis set).

	A		[A,NCS^-]			
	E, Hartree	ZPE, Hartree	E , Hartree	ZPE , Hartree	BSSE, Hartree	ΔE, Hartree
M062X, CH_2Cl_2						
TCB	-601.213202	0.095687	-1092.41656	0.105269	0.001513	-0.009281
TNB	-845.768616	0.109395	-1336.97191	0.119176	0.001531	-0.008993
TCP	-633.264183	0.070713	-1124.47259	0.080446	0.001568	-0.014121
pCA	-2219.850305	0.048263	-2711.05963	0.058322	0.001749	-0.014537
pFA	-778.432196	0.054487	-1269.64121	0.064416	0.001686	-0.014416
pBA	-10675.82383	0.045403	-11167.0335	0.05552	0.001876	-0.014726
oCA	-2219.837354	0.048031	-2711.04898	0.057786	0.001779	-0.01711
TCNE	-447.536044	0.047588	-938.747975	0.057753	0.001524	-0.017258
DDQ	-1485.131269	0.064025	-1976.34898	0.074306	0.001845	-0.022597
M062X, CH_3CN						
TCB	-601.216096	0.095686	-1092.42518	0.10518	0.001509	-0.007131
TNB	-845.770657	0.109327	-1336.98002	0.119057	0.001492	-0.007189
TCP	-633.266849	0.070662	-1124.4802	0.080367	0.001557	-0.011134
pCA	-2219.851584	0.048311	-2711.06721	0.05829	0.001726	-0.012967
pFA	-778.433662	0.05454	-1269.6485	0.064398	0.00167	-0.012357
pBA	-10675.82515	0.045468	-11167.0412	0.055458	0.001854	-0.013277
oCA	-2219.838803	0.048013	-2711.05651	0.057845	0.001763	-0.015154
TCNE	-447.537967	0.047643	-938.754816	0.057713	0.001509	-0.014316
DDQ	-1485.133715	0.064161	-1976.35594	0.074238	0.001832	-0.019364
ωB97XD, CH_2Cl_2						
TCB	-601.200253	0.095528	-1092.41013	0.104919	0.00147	-0.016034
TNB	-845.814464	0.108915	-1337.0236	0.118791	0.001402	-0.014869
TCP	-633.243602	0.070315	-1124.45734	0.079956	0.001525	-0.019583
pCA	-2219.897488	0.047988	-2711.11054	0.057795	0.001678	-0.018587
pFA	-778.462839	0.054115	-1269.67575	0.063907	0.001638	-0.018501
pBA	-10675.91161	0.045315	-11167.1254	0.055089	0.001801	-0.019219
oCA	-2219.88497	0.047709	-2711.10026	0.057392	0.001745	-0.02088
TCNE	-447.518104	0.047267	-938.734573	0.057323	0.001533	-0.021896
DDQ	-1485.147705	0.063704	-1976.36895	0.073789	0.001824	-0.026355
ωB97XD CH_3CN						
TCB	-0.016034	0.095518	-1092.41903	0.105052	0.001463	-0.013823
TNB	-0.014869	0.108847	-1337.03186	0.118529	0.001374	-0.013359
TCP	-0.019583	0.070564	-1124.4653	0.079988	0.001518	-0.016884
pCA	-0.018587	0.048044	-2711.11833	0.057823	0.001657	-0.017131
pFA	-0.018501	0.054167	-1269.68321	0.063845	0.00161	-0.01667
oCA	-0.02088	0.047691	-2711.10791	0.057434	0.001726	-0.019016
TCNE	-0.021896	0.047327	-938.741534	0.057262	0.001521	-0.019004
DDQ	-0.026355	0.063839	-1976.37604	0.073745	0.001806	-0.023132

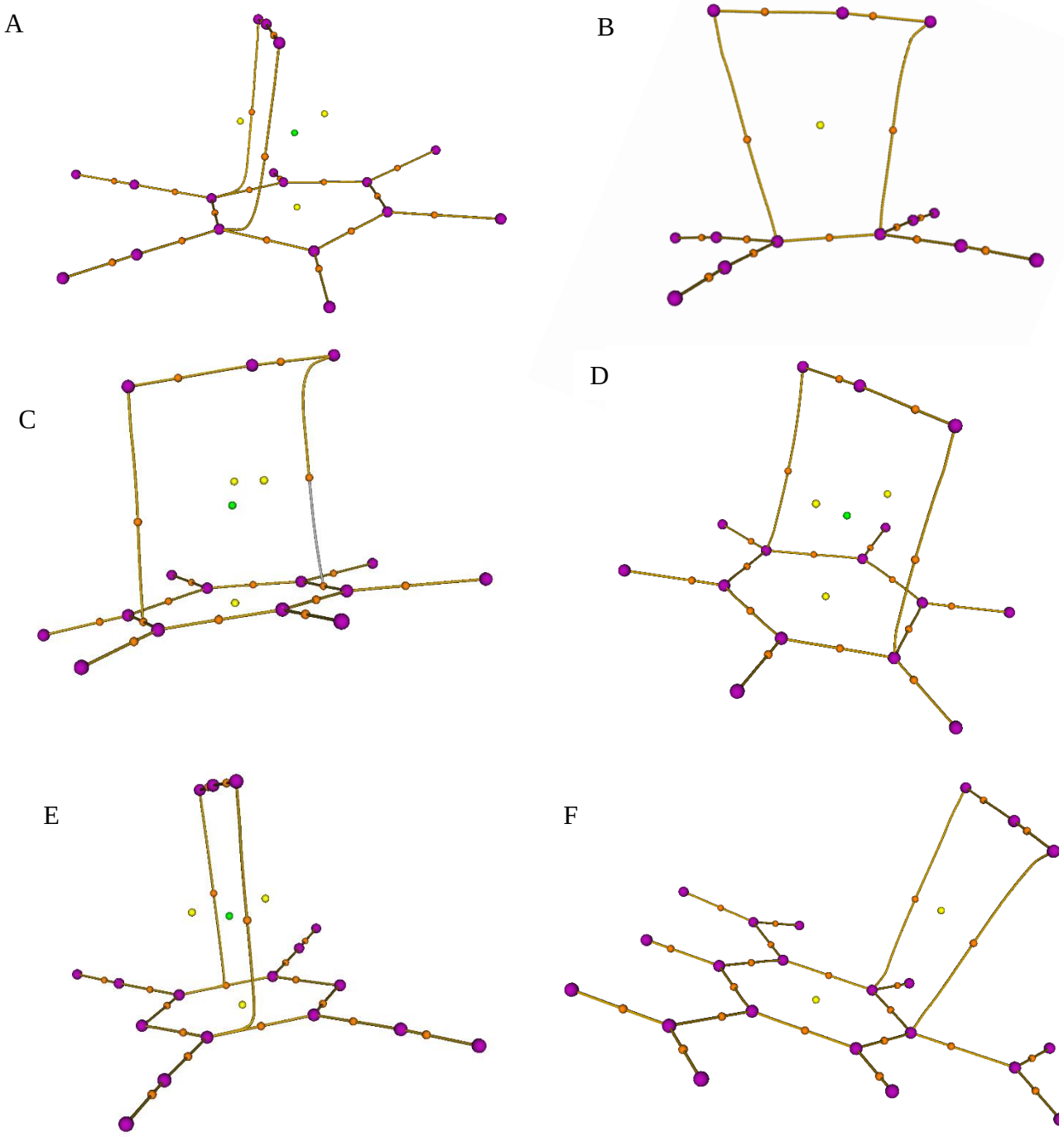


Figure S14. Critical points and bond paths for calculated complexes of thiocyanate with DDQ (A), TCNE (B), oCA (C), pFA (D), TCP (E), and TNB (F). The (3,-1), (3,+1) and (3,+3) CPs are represented by small orange, yellow and green spheres, respectively.

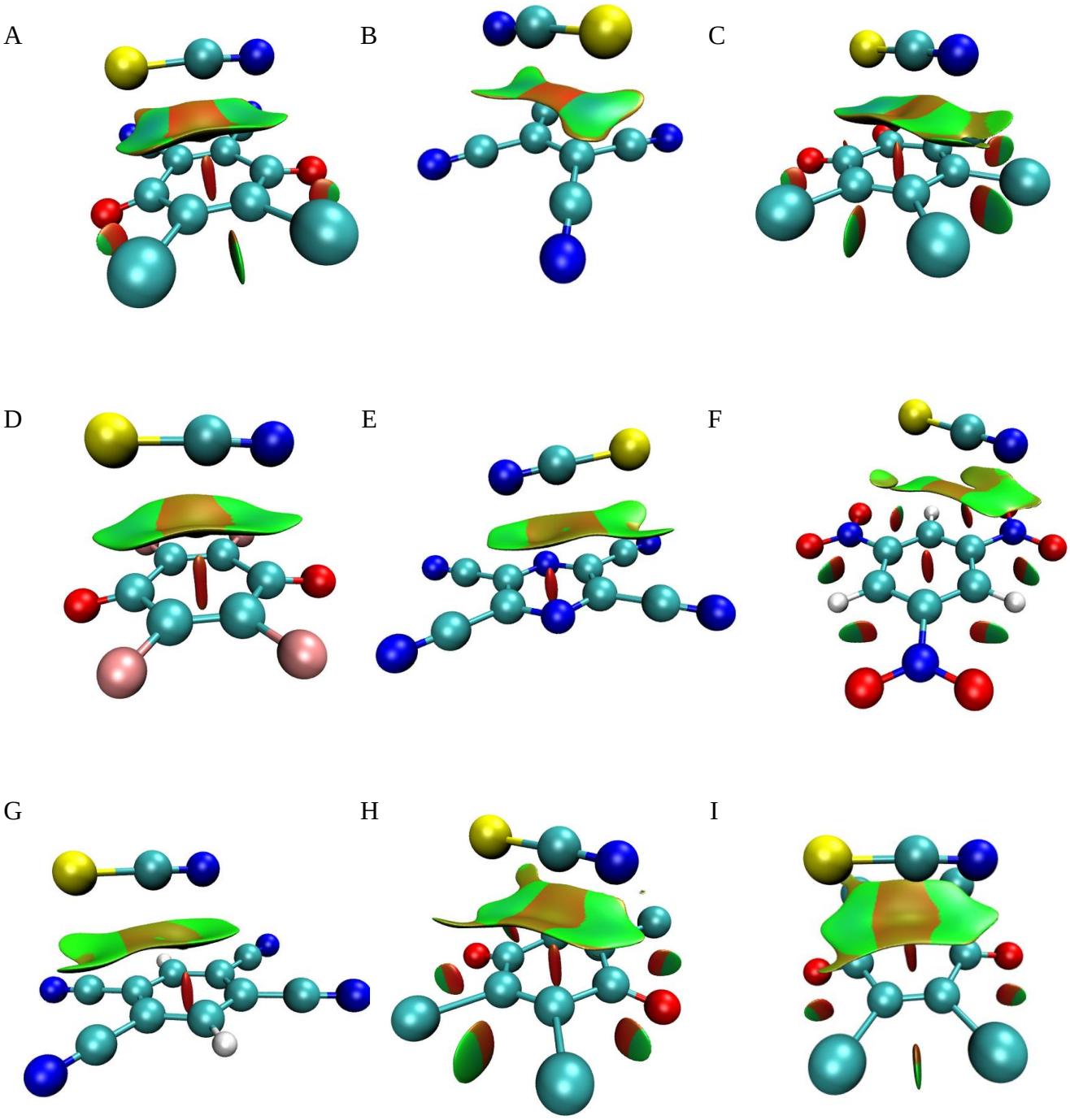


Figure S15. NCI plots paths for calculated complexes of thiocyanate with DDQ (A), TCNE (B), oCA (C), pFA (D), TCP (E), TNB (F). TCB (G), pBA (H) and pCA (I), The gradient cutoff is s = 0.3 a.u. and the color scale is in the range -0.035 < r < 0.02 a.u.

Table S5. Characteristics of the (3,-1) critical points between terminal (N or S) atoms of thiocyanate and π-acceptors in the [A,NCS^-] complexes.[a]

	N•••C bond path			S•••C bond path		
A	ρ	$\nabla^2\rho$	H(r)	ρ	$\nabla^2\rho$	H(r)
TCB	0.00839	0.02869	0.00115	0.00814	0.02467	0.00095
TNB	0.00984	0.03265	0.00123	0.00999	0.02766	0.00096
TCP	0.01134	0.03752	0.00111	0.00966	0.02889	0.00096
pCA	0.01211	0.04229	0.00155	0.01257	0.03459	0.00102
pFA	0.01220	0.04240	0.00155	0.01324	0.03616	0.00103
pBA	0.01217	0.04253	0.00156	0.01240	0.03419	0.00103
oCA	0.01009	0.03377	0.00118	0.01734	0.04320	0.00061
TCNE	0.01517	0.04762	0.00134	0.01655	0.03932	0.00069
DDQ	0.01434	0.04590	0.00128	0.01718	0.04118	0.00050

a) From M062X/def2tzvpp computations in acetonitrile, ρ is the electron density, $\nabla^2\rho$ is Laplacian of electron density, H(r) is the total energy density (in a.u.).

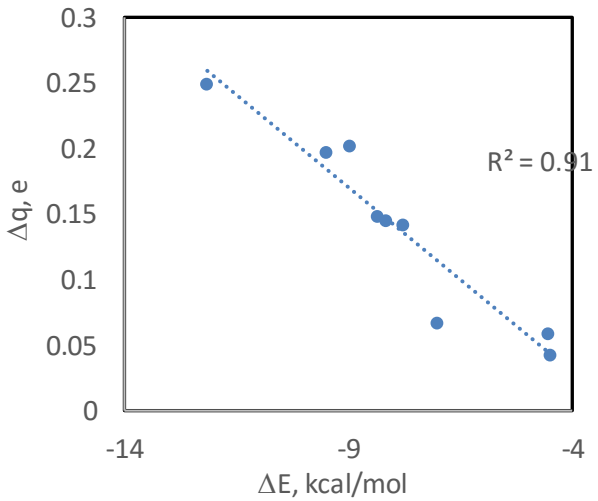


Figure S16. Correlation between interaction energy ΔE (from M062X/def2tzvpp computations in acetonitrile) and charge transfer Δq (from AIM analysis).

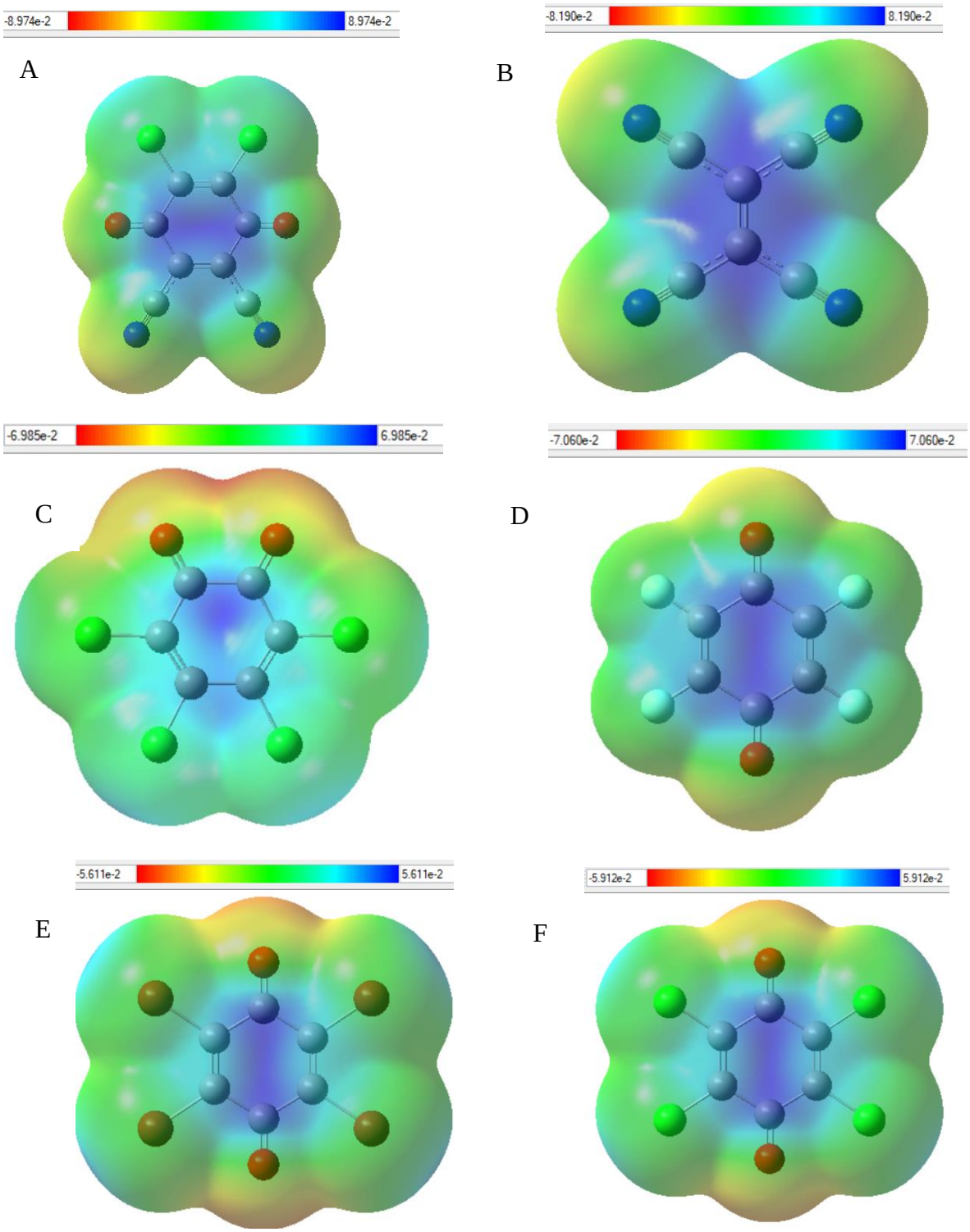


Figure S17. ESP surfaces showing values of most positive and most negative potentials (at 0.001 electron density, in au) for DDQ (A), TCNE (B), oCA (C), pFA (D), pBA (E), pCA (F).

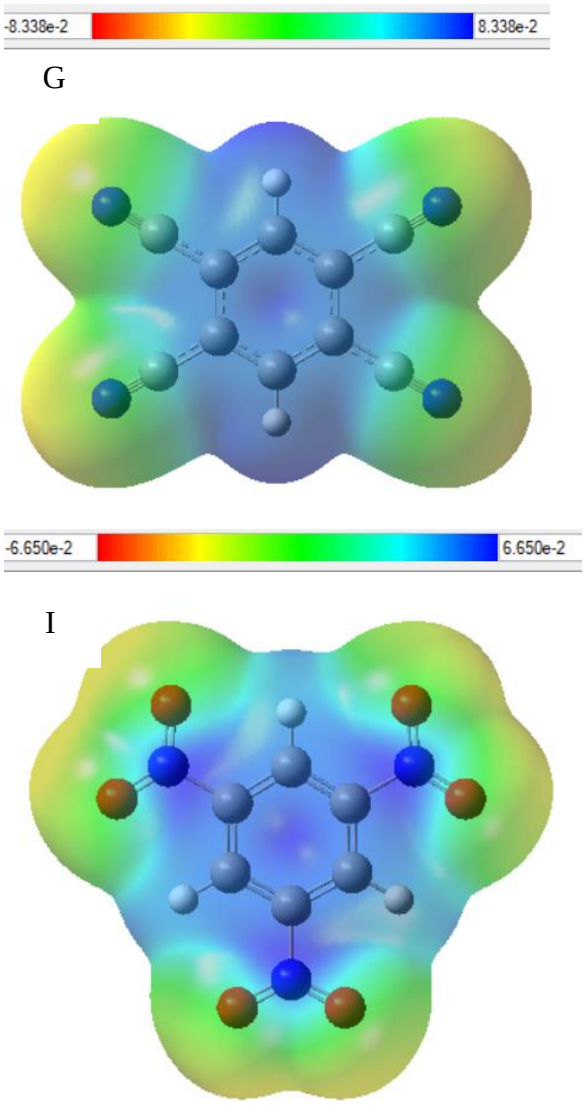


Figure S17 (cont). ESP surfaces showing values of most positive and most negative potentials (at 0.001 electron density, in au) for TCB (G), TCP (H) and TNB (I),

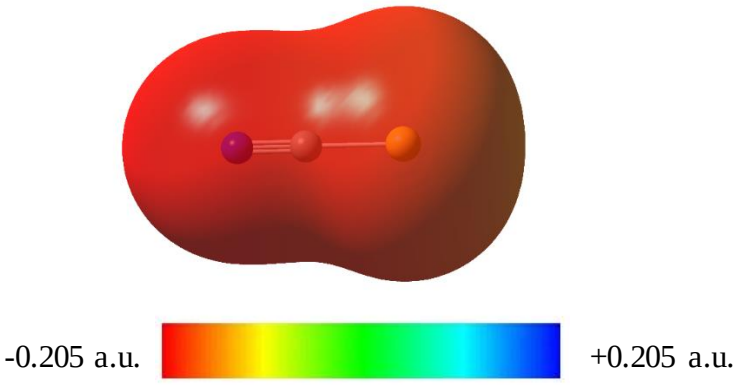


Figure S18. ESP surface of thiocyanate anion (at 0.001 au electron density).

Atomic coordinates of the optimized A•NCS^- complexes (from M062X/def2tzvpp computations)

A	In CH_3CN				In CH_2Cl_2			
DDQ	C	1.55456	-0.01550	-0.26259	C	1.55603	-0.01316	-0.25820
	C	0.79749	1.24555	-0.01265	C	0.79930	1.24682	-0.00499
	C	-0.53190	1.23719	0.18577	C	-0.53089	1.23770	0.19456
	C	-1.31763	-0.03355	0.12119	C	-1.31638	-0.03257	0.12623
	C	-0.51890	-1.29182	0.15902	C	-0.51657	-1.29016	0.16815
	C	0.80855	-1.28289	-0.02600	C	0.81079	-1.28061	-0.01726
	O	2.68950	0.00657	-0.65766	O	2.68683	0.00762	-0.66499
	C	1.55920	2.45493	-0.02123	C	1.55778	2.45814	-0.02152
	N	2.16786	3.42661	-0.03007	N	2.16077	3.43323	-0.04177
	C	-1.28370	2.44138	0.36469	C	-1.28377	2.44248	0.36600
	N	-1.88310	3.41001	0.49381	N	-1.88410	3.41210	0.48326
	O	-2.51191	-0.02296	-0.01431	O	-2.50943	-0.02347	-0.02246
	Cl	-1.41635	-2.72151	0.36583	Cl	-1.41368	-2.72105	0.37369
	Cl	1.74833	-2.70004	-0.05731	Cl	1.75085	-2.69811	-0.04988
	N	1.92141	0.22623	2.50184	N	1.91974	0.21712	2.49626
	C	0.79413	0.23672	2.80260	C	0.79270	0.22827	2.79780
	S	-0.82269	0.26839	3.08707	S	-0.82512	0.26096	3.07512
oCA	C	1.42802	0.12861	0.11500	C	1.42776	0.13051	0.11647
	C	0.59261	1.41320	-0.05209	C	0.59267	1.41488	-0.04697
	C	-0.87625	1.25721	-0.08437	C	-0.87720	1.25829	-0.07216
	C	-1.44971	0.04061	-0.08119	C	-1.45163	0.04204	-0.07328
	C	-0.65081	-1.18776	0.07917	C	-0.65317	-1.18608	0.08172
	C	0.68508	-1.14338	0.22879	C	0.68288	-1.14138	0.23095
	O	2.62694	0.18904	0.06205	O	2.62630	0.18747	0.05227
	O	1.14797	2.46331	-0.23296	O	1.14579	2.46415	-0.23918
	Cl	-1.77375	2.70471	-0.20052	Cl	-1.77497	2.70645	-0.18255
	Cl	-3.14186	-0.11911	-0.24971	Cl	-3.14462	-0.11698	-0.24275
	Cl	-1.47324	-2.68474	0.08558	Cl	-1.47571	-2.68397	0.08104
	Cl	1.63615	-2.53795	0.48359	Cl	1.63407	-2.53743	0.47923
	N	-1.78174	-0.66235	2.96229	N	-1.77532	-0.66706	2.95708
	C	-0.80629	-0.02764	2.97212	C	-0.79996	-0.03215	2.96394
	S	0.58254	0.86671	2.91226	S	0.58880	0.86173	2.89420
pBA	C	1.47176	0.10188	-0.09665	C	1.46237	0.13379	-0.10371
	C	0.60154	1.31201	0.03575	C	0.57642	1.32826	0.06135
	C	-0.72918	1.20796	0.05689	C	-0.75275	1.20503	0.09105
	C	-1.40623	-0.12176	-0.03917	C	-1.41239	-0.13157	-0.02397
	C	-0.53138	-1.32612	0.10138	C	-0.51888	-1.32477	0.09258
	C	0.79941	-1.22321	0.08050	C	0.81024	-1.20245	0.06311
	O	2.63608	0.18771	-0.38097	O	2.61836	0.24043	-0.41435

	Br	1.51559	2.94092	0.07923	Br	1.46779	2.96973	0.12097
	Br	-1.88322	2.67285	0.15576	Br	-1.92681	2.65176	0.21984
	O	-2.58391	-0.21747	-0.25606	O	-2.58863	-0.24034	-0.24285
	Br	-1.44443	-2.94799	0.25431	Br	-1.40812	-2.96191	0.22275
	Br	1.95490	-2.68807	0.17884	Br	1.98740	-2.65263	0.12531
	N	-1.39467	-0.07163	2.81581	N	-1.36560	-0.12861	2.81636
	C	-0.23994	0.02118	2.95270	C	-0.21108	-0.02003	2.94368
	S	1.39816	0.15175	3.06167	S	1.42613	0.13329	3.02788
pCA	C	1.22665	-0.13639	0.26274	C	1.22607	-0.14770	0.27549
	C	0.55817	1.19753	0.21442	C	0.57496	1.19522	0.24643
	C	-0.74183	1.31454	-0.07153	C	-0.72197	1.33372	-0.04467
	C	-1.58192	0.11449	-0.36476	C	-1.57593	0.15035	-0.36505
	C	-0.96866	-1.21461	-0.06655	C	-0.98231	-1.19054	-0.07930
	C	0.33149	-1.33028	0.21906	C	0.31518	-1.32809	0.20966
	O	2.42281	-0.24362	0.29991	O	2.42074	-0.27053	0.30743
	Cl	1.57044	2.53675	0.50039	Cl	1.60530	2.51625	0.55493
	Cl	-1.53453	2.81566	-0.20390	Cl	-1.49140	2.84921	-0.16329
	O	-2.67232	0.21130	-0.86083	O	-2.65556	0.26911	-0.88015
	Cl	-2.01623	-2.55144	-0.19337	Cl	-2.04621	-2.51207	-0.23108
	Cl	1.08907	-2.82715	0.51019	Cl	1.05272	-2.83958	0.47866
	N	0.64078	-0.07959	3.05975	N	0.62495	-0.14876	3.04318
	C	-0.51670	0.02350	2.95959	C	-0.53054	-0.02487	2.94224
	S	-2.14203	0.16931	2.73490	S	-2.15080	0.14828	2.70552
pFA	C	1.27890	0.02769	0.25349	C	1.27673	0.02751	0.25862
	C	0.49225	1.28315	0.16521	C	0.48829	1.28202	0.17442
	C	-0.81298	1.27727	-0.09106	C	-0.81698	1.27573	-0.08354
	C	-1.57106	0.01695	-0.27684	C	-1.57495	0.01592	-0.27326
	C	-0.81760	-1.23264	-0.01507	C	-0.82090	-1.23258	-0.00853
	C	0.48770	-1.22786	0.24073	C	0.48431	-1.22731	0.24971
	O	2.48251	0.02589	0.26548	O	2.48074	0.02539	0.25276
	F	1.18086	2.40183	0.28920	F	1.17599	2.40218	0.29505
	F	-1.50881	2.39096	-0.22537	F	-1.51104	2.39045	-0.22227
	O	-2.71293	0.00757	-0.65691	O	-2.71276	0.00599	-0.66551
	F	-1.51780	-2.34969	-0.08133	F	-1.51822	-2.35156	-0.08072
	F	1.17221	-2.33949	0.43277	F	1.16849	-2.34033	0.43770
	N	-2.10126	0.09040	2.52496	N	-2.09086	0.10044	2.51671
	C	-0.99035	0.10506	2.87939	C	-0.97995	0.10866	2.87136
	S	0.60340	0.12289	3.29535	S	0.61617	0.11748	3.27750
TCB	C	1.39932	0.08918	0.00401	C	1.40133	0.09748	0.00472
	C	0.70003	1.28432	-0.04746	C	0.70147	1.29235	-0.04718
	C	-0.70123	1.28431	-0.04815	C	-0.69976	1.29070	-0.03529
	C	-1.40009	0.08890	0.00384	C	-1.39485	0.09411	0.03401
	C	-0.69930	-1.10833	0.05967	C	-0.69292	-1.10297	0.08229
	C	0.69885	-1.10827	0.05965	C	0.70444	-1.10175	0.06404

	H	2.47872	0.08952	0.00925	H	2.48084	0.09924	0.00312
	C	1.41802	2.52465	-0.11016	C	1.42177	2.53082	-0.12530
	N	1.99360	3.51275	-0.19295	N	2.00459	3.51355	-0.21942
	C	-1.41869	2.52472	-0.11381	C	-1.42465	2.52648	-0.11467
	N	-1.99350	3.51312	-0.19739	N	-2.01138	3.50546	-0.22212
	H	-2.47946	0.08812	0.01015	H	-2.47417	0.09262	0.05344
	C	-1.41878	-2.34552	0.15341	C	-1.41278	-2.34038	0.16686
	N	-1.98926	-3.33681	0.23245	N	-1.98905	-3.32964	0.22719
	C	1.41844	-2.34559	0.15391	C	1.42877	-2.33742	0.12983
	N	1.98892	-3.33688	0.23266	N	2.00834	-3.32561	0.17458
	N	0.00182	-0.40052	3.06911	N	0.11704	-0.40196	3.07217
	C	0.00174	0.76350	3.13087	C	-0.00003	0.75644	3.12877
	S	0.00162	2.41883	3.19095	S	-0.16776	2.40313	3.18055
TCNE	C	1.38953	-0.02036	-0.09871	C	1.39176	-0.02002	-0.08068
	C	-0.70476	1.20133	-0.04134	C	-0.70457	1.20094	-0.03378
	N	-1.28406	2.19018	-0.06278	N	-1.28465	2.18915	-0.06950
	C	-0.70130	-1.24934	-0.07658	C	-0.70137	-1.24805	-0.06740
	N	-1.27770	-2.23889	-0.12599	N	-1.27965	-2.23586	-0.13163
	C	2.12292	1.20817	-0.17227	C	2.12474	1.20799	-0.16781
	N	2.69214	2.19651	-0.28567	N	2.69511	2.19354	-0.29998
	C	2.12687	-1.24399	-0.20698	C	2.12962	-1.24242	-0.20009
	N	2.69938	-2.22692	-0.34758	N	2.70473	-2.22169	-0.35615
	C	0.03473	-0.02295	-0.05910	C	0.03540	-0.02271	-0.04313
	C	0.48297	-0.06454	2.82492	C	0.47861	-0.06693	2.81973
	N	-0.67765	-0.06797	2.70478	N	-0.68175	-0.06895	2.69737
	S	2.12665	-0.05773	2.86315	S	2.12173	-0.06147	2.84889
TCP	C	1.53846	-0.06927	-0.30897	C	1.55008	-0.07293	-0.28722
	N	0.91775	1.08394	-0.11817	N	0.94464	1.08640	-0.08036
	C	-0.38363	1.03245	0.09321	C	-0.35778	1.05058	0.12545
	C	-1.08008	-0.18813	0.09732	C	-1.07280	-0.15994	0.10179
	N	-0.46338	-1.33544	-0.11275	N	-0.47171	-1.31199	-0.12525
	C	0.84467	-1.28416	-0.30772	C	0.83915	-1.27707	-0.30842
	C	2.96560	-0.03750	-0.49965	C	2.97664	-0.05662	-0.48236
	N	4.10084	-0.03814	-0.65007	N	4.11009	-0.06731	-0.64602
	C	-1.07975	2.27761	0.30069	C	-1.03816	2.30313	0.34148
	N	-1.65135	3.26138	0.43039	N	-1.59679	3.29497	0.46671
	C	-2.50491	-0.22144	0.31422	C	-2.50184	-0.17399	0.29082
	N	-3.64153	-0.22875	0.45336	N	-3.64248	-0.16667	0.39284
	C	1.54162	-2.52985	-0.49884	C	1.51851	-2.52845	-0.52304
	N	2.11796	-3.50777	-0.65045	N	2.07985	-3.51066	-0.70118
	N	1.31964	-0.74312	2.60323	N	1.28275	-0.80752	2.59924
	C	0.35967	-0.18067	2.95156	C	0.32213	-0.24590	2.94716
	S	-1.01415	0.62445	3.40263	S	-1.05480	0.55956	3.38836
TNB	C	1.00322	-0.08839	0.19798	C	1.00681	-0.06865	0.20253

	C	0.31857	1.10149	0.05855	C	0.32184	1.11971	0.05255
	C	-0.98105	1.02321	-0.40879	C	-0.97834	1.03633	-0.41567
	C	-1.59731	-0.16766	-0.72692	C	-1.59546	-0.15788	-0.71612
	C	-0.84982	-1.32109	-0.57049	C	-0.84857	-1.31061	-0.54562
	C	0.45010	-1.31620	-0.10865	C	0.45183	-1.29987	-0.08604
	N	2.38266	-0.04776	0.71052	N	2.38679	-0.02299	0.71266
	O	2.99174	-1.09025	0.75704	O	3.00890	-1.05884	0.73212
	O	2.82131	1.02844	1.04075	O	2.81251	1.05140	1.06392
	H	0.77105	2.04638	0.30936	H	0.77526	2.06653	0.29345
	N	-1.74936	2.27109	-0.54554	N	-1.74572	2.28249	-0.56807
	O	-1.16521	3.30948	-0.34585	O	-1.16412	3.32212	-0.36838
	O	-2.91719	2.17819	-0.84586	O	-2.91008	2.18737	-0.88269
	H	-2.61526	-0.19926	-1.08136	H	-2.61461	-0.19336	-1.06658
	N	-1.47330	-2.61295	-0.90625	N	-1.47330	-2.60556	-0.86379
	O	-2.61193	-2.59385	-1.31141	O	-2.61635	-2.59133	-1.25802
	O	-0.80713	-3.61004	-0.75646	O	-0.80403	-3.60072	-0.71452
	H	1.00792	-2.23044	0.01771	H	1.00848	-2.21242	0.05662
	N	0.83783	-0.55060	3.24665	N	0.78537	-0.65762	3.18665
	C	0.29920	0.48304	3.22696	C	0.27965	0.39283	3.18127
	S	-0.45845	1.95212	3.15612	S	-0.42927	1.88604	3.11781