Supporting Information

The Amino-tetracyanocyclopentadienide system: Light-induced formation of a thermally stable Cyclopentadienyl Radical

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1. Crystallography

The structures of **1b** and **2** were determined on a BRUKER D8-Venture diffractometer TXS system equipped with a multilayer mirror optics monochromator and a Mo Kα rotating-anode X-ray tube. The structures were solved with SHELXT as included in the WINGX program package,[1] and refined with SHELXL version 2014/7. Since both compounds showed in the PLATON analysis large solvent accessible voids, the data were treated with the SQUEEZE routine of PLATON and refined correspondingly.

Table S 1: Experimental Details of the Crystal Structure Determinations

Identification code	**1b**	**2**
Empirical formula	$C_9H_6N_6$	$C_9H_2N_5$
Formula weight	198.20	180.16
Temperature	100(2)	123(2)
Crystal system	Triclinic	Monoclinic
Space group	P -1	P 2_1/m
Unit cell dimensions		
a [Å]	6.7736(3)	3.9752(3)
b	8.6454(4)	26.0148(19)
c	10.2350(4)	6.2820(5)
α [°]	67.6660(10)	90
β	72.808(2)	97.357(3)
γ	83.739(2)	90
Volume [$Å^3$]	529.63(4)	644.30(9)
Z	2	2
ρ_{calc} [g/cm^3]	1.243	0.929
μ [mm^{-1}]	0.085	0.063
F(000)	204	182
Crystal size [mm^3]	0.09 x 0.06 x 0.02	0.03 x 0.02 x 0.02
Theta range for data collection	2.706 to 26.391°.	3.132 to 25.353
Index ranges	-7≤h≤8, -10≤k≤10, -12≤l≤12	-4≤h≤4, -31≤k≤31, -7≤l≤7
Reflections collected	6157	6744
Independent reflections	2136 [R(int) = 0.0305]	1213 [R(int) = 0.0536]
Absorption correction	Semi-empirical	
Max. and min. transmission	0.9705 and 0.847	0.862 and 0.7953
Data / parameters	2136/ 149	1213/ 73
Goodness-of-fit on F^2	1.019	1.051
R1/ wR2 [I>2sigma(I)]	0.0549/ 0.1354	0.0826/0.2233
R1/ wR2 (all data)	0.0685/ 0.1425	0.0942/ 0.2319
Largest diff. peak and hole [e $Å^{-3}$]	0.443 and -0.249	0.1231 and -0.093
CCDC-#	1909580	1909579

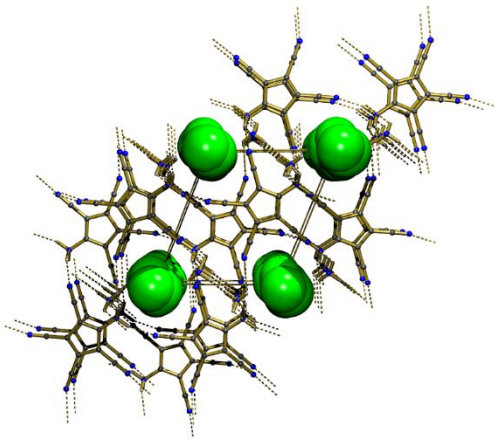


Figure S 1: PLATON Cavity plot of **1b**

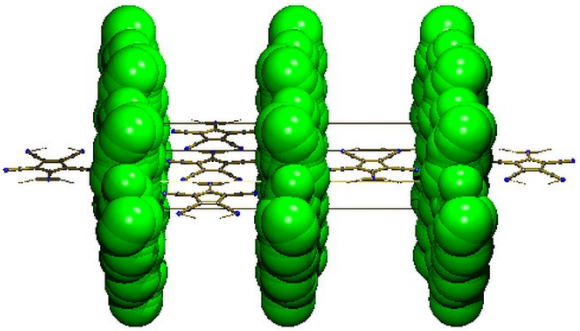


Figure S 2: PLATON Cavity plot of **2**

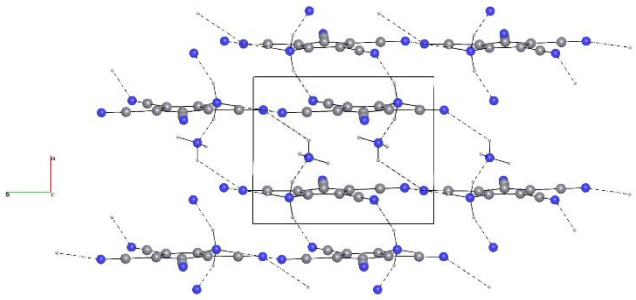


Figure S 3: packing diagram of **1c** including hydrogen bonds, viewed down *c*. N0–H0B–N4: N0…N4 (*x,y,z-1*): 2.91Å; N1–H2–N2: N1…N2(*2-x, 1-y, -z*): 2.93 Å; N1–H1–N3: N1…N3(*x,y-1,z*): 2.93 Å.

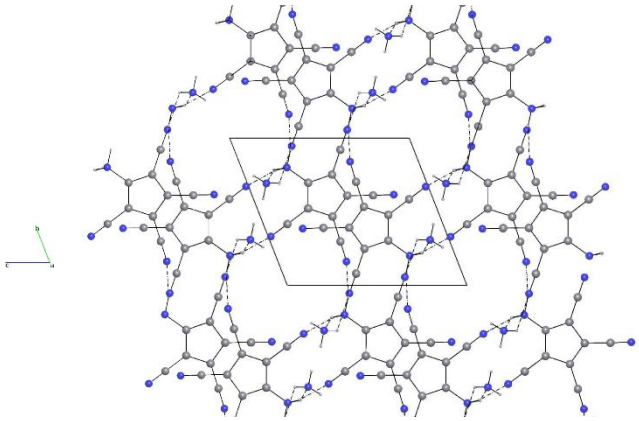


Figure S 4: packing diagram of **1c** including hydrogen bonds, watched down *a*. N0–H0B–N4: N0…N4 (*x,y,z-1*): 2.91Å; N1–H2–N2: N1…N2(*2-x, 1-y, -z*): 2.93 Å; N1–H1–N3: N1…N3(*x,y-1,z*): 2.93 Å

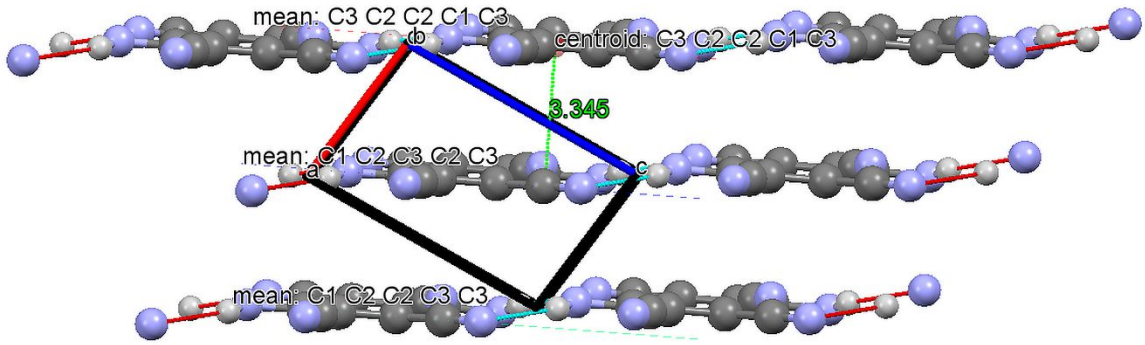


Figure S 5: packing diagram of **2** including hydrogen bonds, viewed down *b*.

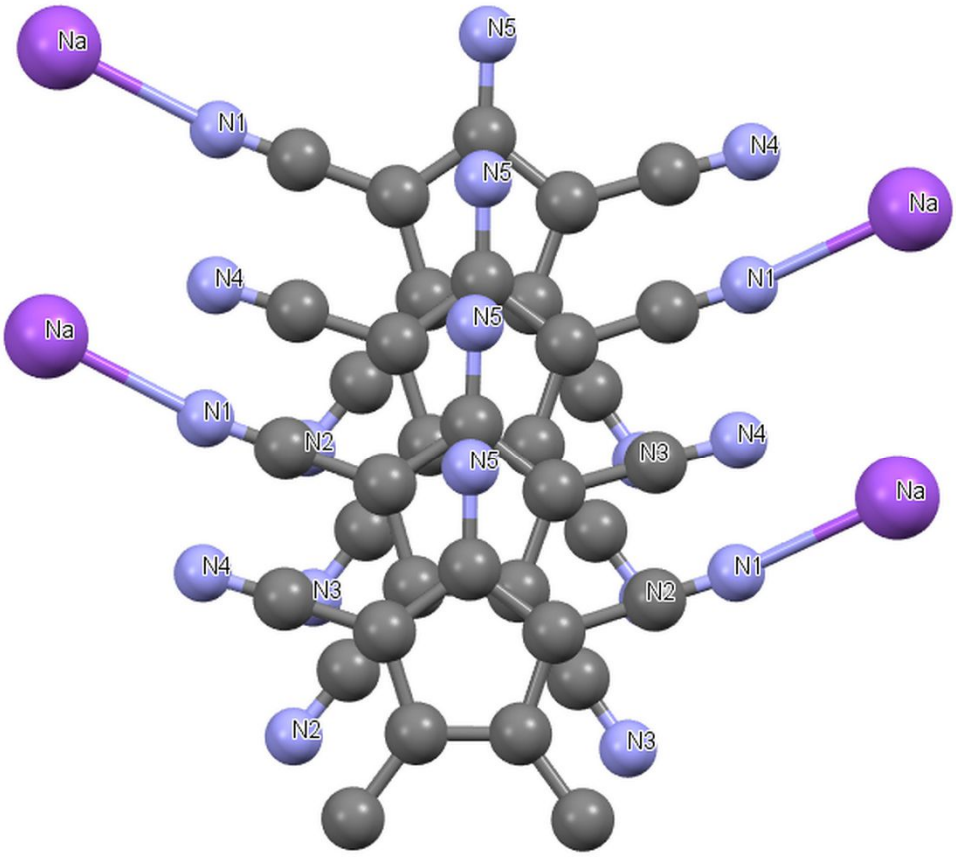


Figure S 6: Stacking of the ATCC rings in Na(ATCC) [ ], viewed perpendicular to the ring planes (H-atoms omitted)

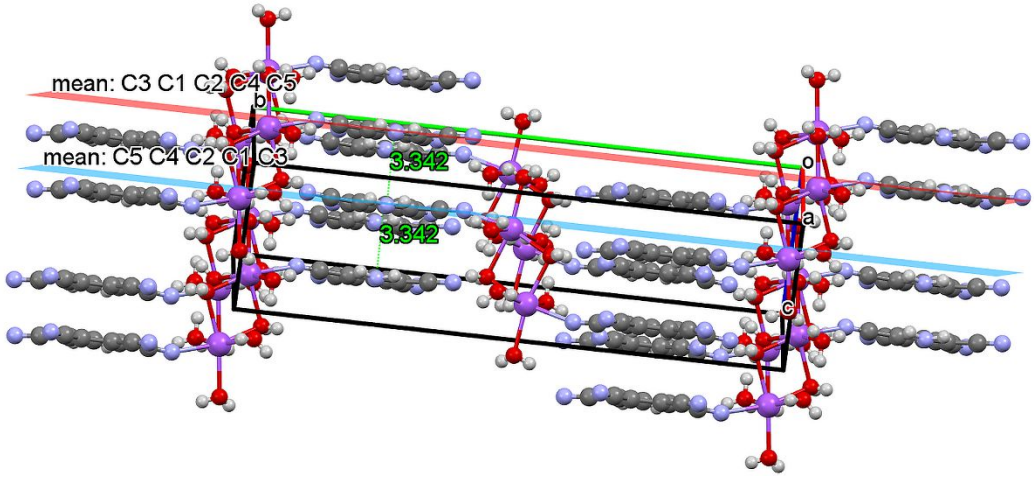


Figure S 7: Stacking of the ATCC rings in Na(ATCC) [ ], viewed parallel to the ring planes.

2. Cyclovoltammetry.

CV measurements were performed with an Autolab potentiostat/galvanostat (PGSTAT302N) with a FRA32M module operated with Nova 1.11 software and a conventional three electrode setup. Two platinum wires were used as working and as counter electrode, respectively. An Ag/ 0.01M $AgNO_3$ electrode was utilized as reference electrode.

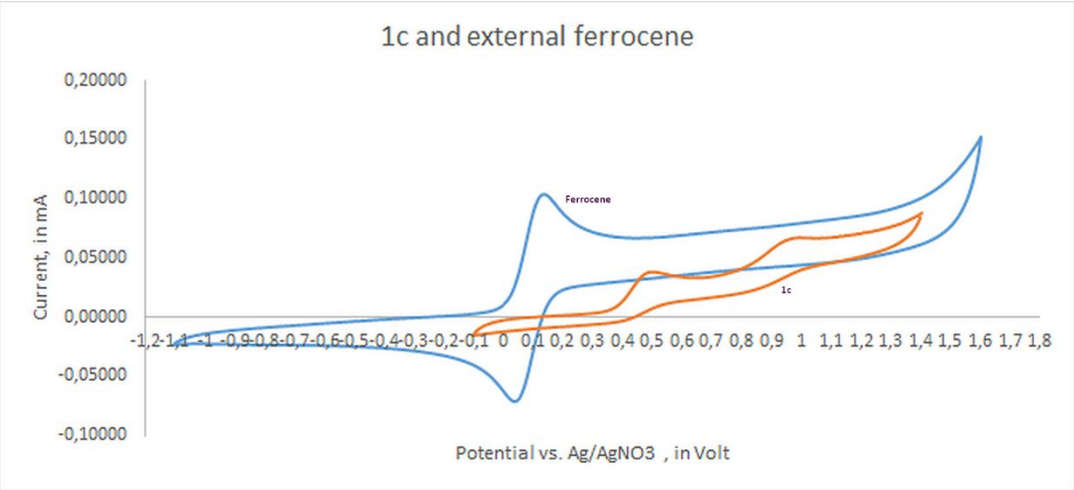


Figure S 8: Cyclovoltammogram of **1c** with external ferrocene

3. DFT calculations:

All of the *ab-initio* calculations were computed using functional density level of theory as implemented in the Gaussian16 program package.[2] As a consequence of the computational screening study of Ilawe *et al.* for several ionic liquids, the range-separated, dispersion-corrected functional *ω*B97XD were applied with the 6-311++G** basis set.[3] The geometries were optimized and the local minima structures were verified with a harmonic vibrational frequency analysis. The thermochemistry output of the frequency analysis was used for the calculation of the reaction's enthalpy and Gibbs free energy. UV/Vis spectra were calculated with time-dependent density functional theory (TD-*ω*B97XD) and 6-311++G** basis set. Solvent effects were simulated with the Polarizable Continuum Model (PCM) in acetonitrile.

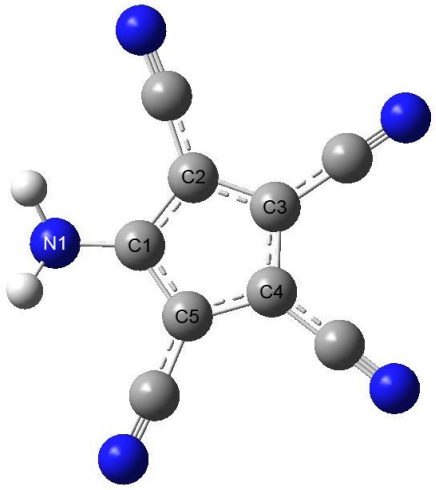
3.1. Energy calculations

Table S 2: Energetics of the zwitterion **1a**

	Gas-phase	**Solution in MeCN**
E_{tot} [a.u.]	−618.336811	−618.388467
E_{HOMO} [a.u.]	−0.34205	−0.33057
E_{LUMO} [a.u.]	-0.02820	−0.01094
ΔE [a.u.]	0.31385	0.31963
ΔE [eV]	8.54	8.70

3.2. Geometry calculations

Table S 3: Calculated Bond Lengths [Å] for the anion of **1c**, the zwitterion **1a** and the radical **2** in MeCN solution, in comparison to the bond lengths found in the crystals of **1b** and **2**



Bond	**Anion**	**Zwitterion**	**Radical**	**1b (X-ray)**	**2 (X-ray)**
C1-C2	1.40883	1.39540	1.43829	1.398(3)	1.403(5)
C2-C3	1.42757	1.41594	1.38464	1.416(3)	1.438(5)
C3-C4	1.39470	1.40134	1.43828	1.398(3)	1.398(8)
C4-C5	1.42757	1.41587	1.38464	1.416(3)	1.438(5)
C5-C1	1.40883	1.39612	1.43829	1.392(3)	1.403(5)
C1-N1	1.37802	1.45395	1.31778	1.445(3)	1.372(7)

3.3. Calculation of UV spectra

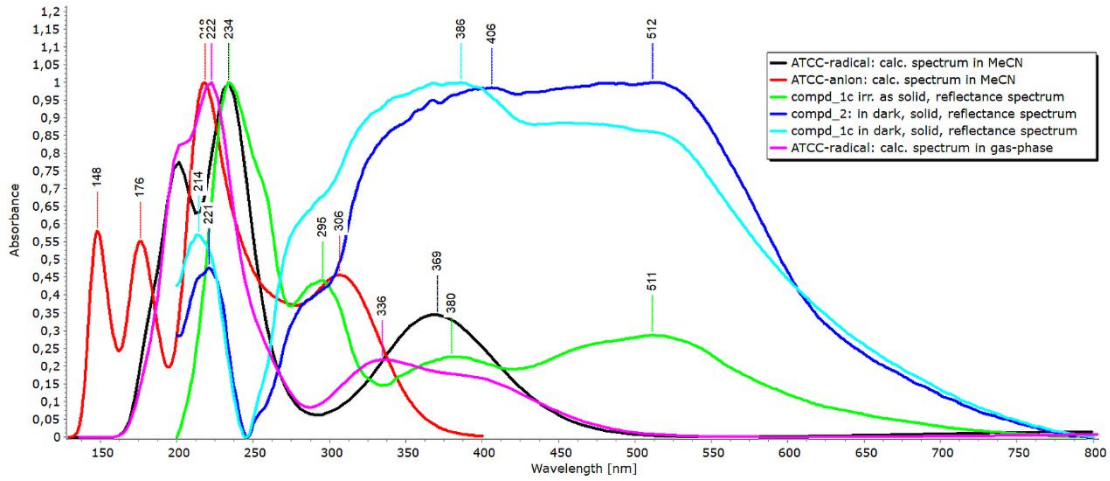


Figure S 9: Calculated UV-VIS spectra of ATCC radical and anion together with observed reflectance spectra of 1c and 2.

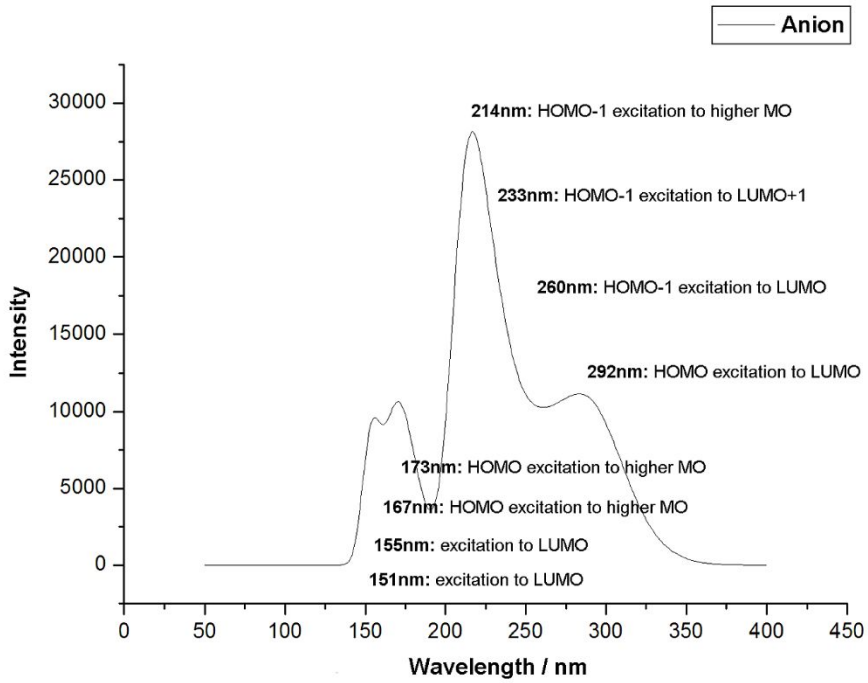


Figure S 10: Band assignments fort he calculated gas phase UV-VIS spectrum of the ATCC anion

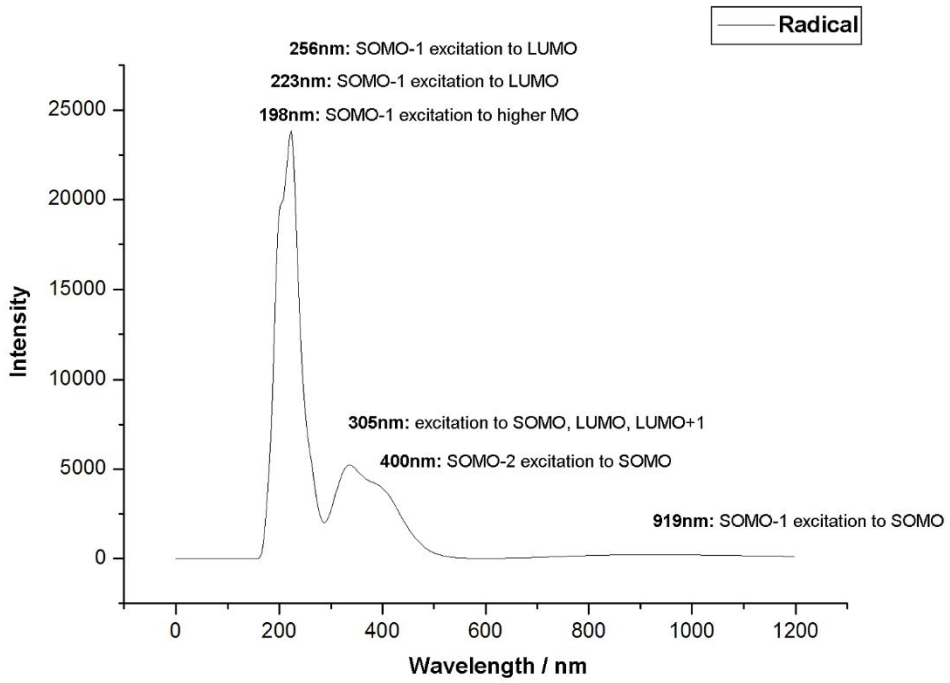
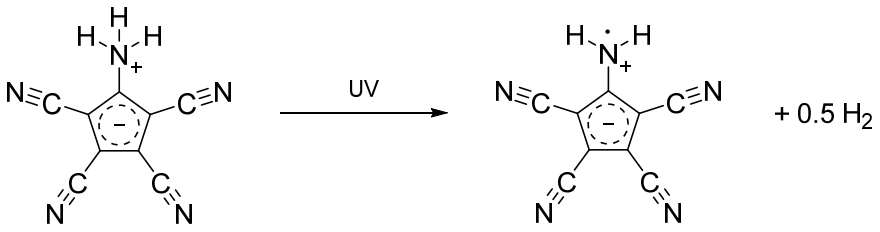


Figure S 11: Band assignments for the calculated gas phase UV-VIS spectrum of the ATCC radical.

3.4. Enthalpies and Free Energies of Reaction

The radical is presumably formed by irradiation of the zwitterion according to the following equation:



The thermochemistry output of harmonic vibrational frequency analysis of the minimum structures of zwitterion, radical and hydrogen can be exploited to determined enthalpy of reaction $\Delta_r H°$, entropy of reaction $\Delta_r S°$ and Gibbs free energy of reaction $\Delta_r G°$ at 298.15 K and 1 atm.

Table S 4: Thermal enthalpy and thermal free energy of the minimum structures of zwitterion, radical and hydrogen as obtained in harmonic vibrational frequency analysis.

	zwitterion	radical	hydrogen
($\varepsilon_o + H_{corr}$) / a.u.	–618.214957	–617.630909	–1.162680
($\varepsilon_o + G_{corr}$) / a.u.	–618.268974	–617.683934	–1.177476
S_{corr} / cal mol^{-1} K^{-1}	113.690	111.600	31.141

The enthalpy of reaction $\Delta_r H^o$ can be calculated by:

$$\Delta_r H^o(298.15\ \mathrm{K}, 1\ \mathrm{atm}) = \sum(\varepsilon_o + H_{corr})_{products} - \sum(\varepsilon_o + H_{corr})_{reactants}$$

The entropy of reaction $\Delta_r S^o$ can be calculated by:

$$\Delta_r S^o(298.15\ \mathrm{K}, 1\ \mathrm{atm}) = \sum (S_{corr})_{products} - \sum (S_{corr})_{reactants}$$

The Gibbs free energy of reaction $\Delta_r G^o$ can be calculated by:

$$\Delta_r G^o(298.15\ \mathrm{K}, 1\ \mathrm{atm}) = \sum (\varepsilon_o + G_{corr})_{products} - \sum (\varepsilon_o + G_{corr})_{reactants}$$

Table S 5: Enthaply of reaction $\Delta_r H°$ and Gibbs free energy of reaction $\Delta_r G°$ of the formation of radical.

	zwitterion → radical
$\Delta_r H°$ / a.u.	0.002708
$\Delta_r H°$ / kJ mol^{-1}	7.11
$\Delta_r G°$/ a.u.	–0.003698
$\Delta_r G°$ / kJ mol^{-1}	–9.71
$\Delta_r S°$ / cal mol^{-1} K^{-1}	13.4805
$\Delta_r S°$ / J mol^{-1} K^{-1}	56.41

References

1 (a) WINGX: L.J. Farrugia, *J. Appl. Cryst*. **1999**, *32*, 837; (b) MERCURY: C.F. Macrae, P.R. Edgington, P. McCabe E. Pidcock, G.P. Shields, R. Taylor, M. Towler, J. van der Streek, *J. Appl. Cryst*. **2006**, *39*, 453; (c) SHELX: G.M. Sheldrick,. *Acta Crystallogr., Sect. A* **2008**, *64*, 112.

2 Gaussian 16, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian Inc., Wallingford CT, **2016**.

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