SUPPORTING INFORMATION

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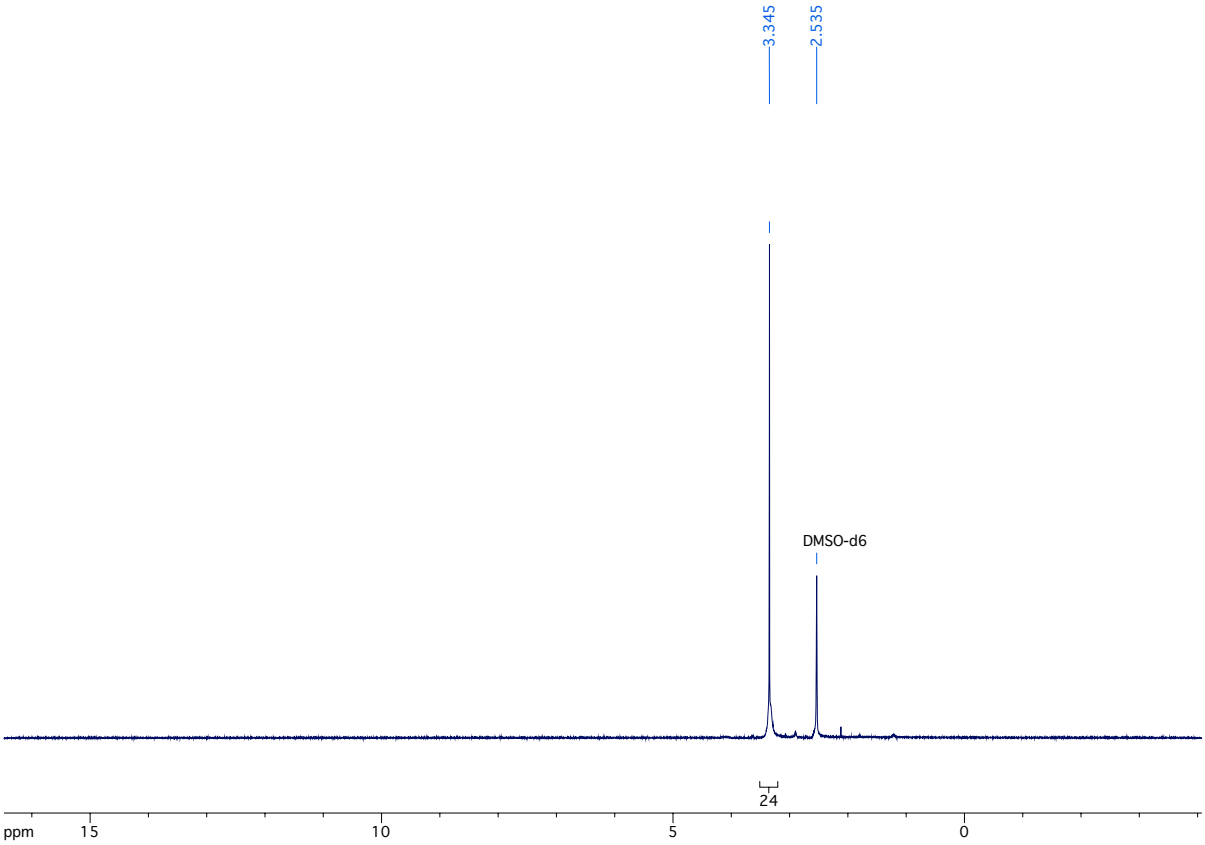
General considerations: Reactions were performed under an atmosphere of argon by using standard Schlenk or dry box techniques; solvents were dried over sodium or CaH_2. Compound **2** was synthesized according to the literature procedure.[1] NMR spectra were performed on the NMR-ICMG platform of Grenoble with an Avance III 400 MHz Brucker spectrometer at room temperature. ^{1}H NMR and ^{13}C NMR chemical shifts (δ) are reported in parts per million (ppm) relative to TMS and were referenced to the residual solvent peak. NMR multiplicities are abbreviated as follows: s = singlet, br = broad signal. Melting points were measured with a Büchi B-545 melting point apparatus system. Crystallographic studies were performed on the RX-ICMG platform of Grenoble with a Bruker AXF-APEXII X-ray diffraction instrument (with Mo/Kα-radiation). Infrared spectra were recorded on a Thermo Scientific Nicolet iS10 FT-IR ATR spectrometer.

Electrochemical measurements were conducted in a standard one-compartment, three-electrode electrochemical cell with a Bio-logic SP-300 potentiostat. Electrochemical reduction was monitored with a Zeiss MCS 501 UV-NIR spectrophotometer. Isotropic EPR spectra were obtained at room temperature on a X-band Brüker EMX Plus spectrometer.

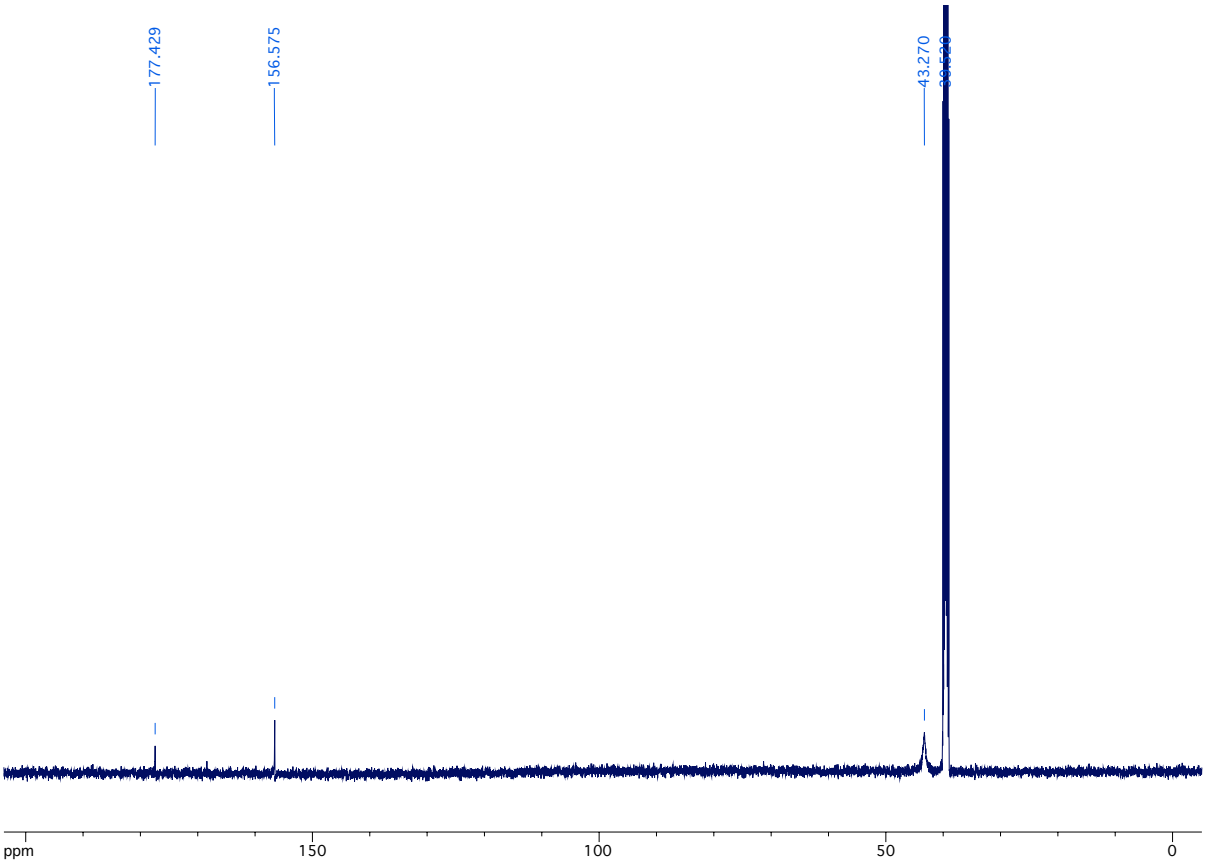
Synthesis of bis(hexafluorophosphate) salt of 1^{2+}: A dichloromethane (DCM) solution (27 mL) of *m*-CPBA (freshly dried with Na_2SO_4; 1.50 g, 8.7 mmol) was added dropwise at room temperature to a solution of **2** (1.50 g, 2.9 mmol) in DCM (15mL). After stirring for an additional 30 minutes, a supernatant was removed by filtration. The remaining yellow solid was dried under vacuum. Extraction with diethyl ether (8 mL x 3) and removal of volatiles *in vaccuo* afforded salt $\mathbf{1}^{2+}$ as a yellow powder. (620 mg, 29 % yield). Crystals suitable for an X-ray study were obtained by recrystallization in hot acetonitrile. mp 196-197°C (decomp.). ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 3.30 (br s, 24H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 43.3 (CH_3), 156.6 (NCN), 177.4 (CO). IR (ν_{max}/cm^{-1}): 1647 (CO). UV-vis (acetonitrile, λmax/nm): 241 and 351 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 8692 and 3331). HRMS: m/z calcd. for $C_{11}H_{24}N_4OPF_6^+$: 373.1592 $[M+PF_6]^+$, found: 373.1581; m/z calcd. for $C_{11}H_{24}N_4O^{2+}$: 114.0970 $[M]^{2+}$, found: 114.0977.

1. A. Fürstner, M. Alcazaro, H. Krause, *Org. Synth.* **2009**, 298.

^{1}H NMR spectrum of $1^{2+}\bullet(PF_6^-)_2$ in DMSO-*d_6* (400 MHz).



^{13}C NMR spectrum of $1^{2+}\bullet(PF_6^-)_2$ in DMSO-*d_6* (100 MHz).



Crystal data for $1^{2+}\bullet(PF_6^-)_2$: $C_{5.5}H_{12}N_2O_{0.5}PF_6$, M = 259.14, monoclinic, a = 16.155(3)Å, b = 6.7318(13) Å, c = 19.587(4)Å, α = 90°, β = 109.09(3)°, γ = 90°, V = 2013.0(7) Å^3, T = 200(0) K, space group *C2/c*, Z = 8, μ(MoKα) = 0.71073 mm^{-1}, 2935 reflections measured (R_{int} = 0.0556). The final $wR(F^2)$ values were 0.1491 ($I > 2\sigma(I)$). The final R_1 values were 0.061 (all data). The final $wR(F^2)$ values were 0.1557 (all data). The goodness of fit on F^2 was 1.036. CCDC 1496180.

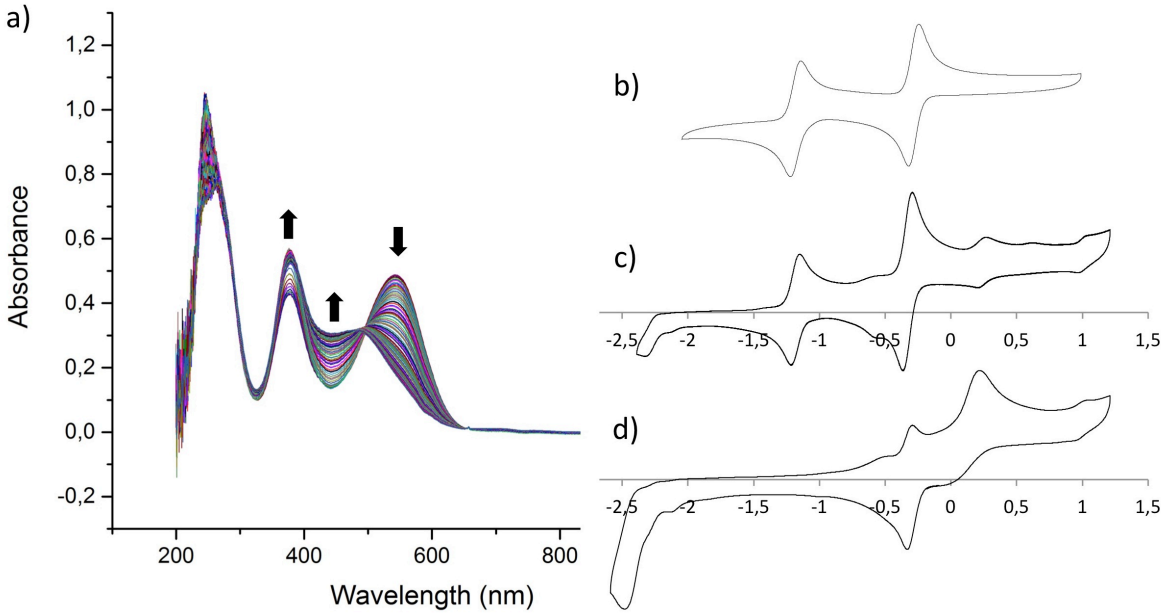


Figure S1: a) UV-vis monitoring (1 scan per 20 seconds) of electrochemical reduction of at -1.80 V on a reticulated vitreous carbon electrode of a 10^{-3} M solution of $\mathbf{1}^{\bullet+}$ and 0.1 M of $Bu_4N\bullet PF_6$ in acetonitrile; b) cyclic voltammogram of a 10^{-3} M solution of $\mathbf{1}^{\bullet+}$ and 0.1 M of $Bu_4N\bullet PF_6$ in acetonitrile at 100 mV.s^{-1} rate (before electrolysis); c) cyclic voltammogram after electrolysis; c) cyclic voltammogram after full decomposition.

DFT Calculations: The DFT calculations were carried at the B3LYP/TZVP level of theory, using the program package Gaussian09.[2] Optimized structures were identified as energy minima by calculating the vibrational frequencies. E is the absolute electronic energy with zero point energy correction (in hartrees).

Cartesians coordinates for the optimized geometry of $\mathbf{1}^{2+}$ (*in vaccuo*)

(E = -727.121278)

Atom	x	y	z
C	1.34760900	0.14063900	0.17640400
C	-1.34765600	0.14058600	-0.17640200
C	-0.00004400	0.88928400	0.00004200
C	2.41861600	-2.00642200	0.80470600
H	3.16641100	-1.94272300	1.59488700
H	2.89770200	-1.95165100	-0.16750300
H	1.91017100	-2.96694000	0.89215400
C	0.43360300	-1.20110300	2.02817200
H	-0.14688600	-2.10289800	1.83276800
H	-0.22502300	-0.35135700	2.18262400
H	0.99545300	-1.34080600	2.95343000
C	3.78140900	0.52676000	0.13323900
H	4.25547900	1.50641500	0.08506400
H	4.36282700	-0.16994400	-0.47012200
H	3.75581700	0.20543400	1.16880000
C	2.35471200	1.61263900	-1.55352300
H	2.56019200	2.63057400	-1.22522200
H	1.39299200	1.58569800	-2.05298700
H	3.12357600	1.29673400	-2.25818100
C	-0.43338400	-1.20111400	-2.02805800

Atom	x	y	z
H	0.14716500	-2.10285400	-1.83257500
H	0.22518200	-0.35131200	-2.18246000
H	-0.99512900	-1.34089000	-2.95336900
C	-2.41841900	-2.00660300	-0.80473300
H	-3.16616900	-1.94302500	-1.59496800
H	-2.89757800	-1.95186000	0.16744200
H	-1.90985400	-2.96706300	-0.89211500
C	-2.35492900	1.61250700	1.55349600
H	-2.56038800	2.63044900	1.22520400
H	-1.39325500	1.58556200	2.05304700
H	-3.12385500	1.29657700	2.25807600
C	-3.78147500	0.52667500	-0.13340700
H	-3.75581000	0.20542900	-1.16898900
H	-4.25556500	1.50631700	-0.08519200
H	-4.36292100	-0.17008400	0.46986400
N	1.38760600	-0.95611000	0.93260400
N	2.40747300	0.69304700	-0.39232100
N	-1.38752000	-0.95617500	-0.93259400
N	-2.40758000	0.69295100	0.39226100
O	-0.00008000	2.08564300	0.00013300

2. *Gaussian 09*, 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 a,d D. J. Fox, Gaussian Inc., Wallingford CT, 2009.

Cartesians coordinates for the optimized geometry of $1^{\bullet+}$ (*in vaccuo*)

(E = -727.472490)

Atom	x	y	z
C	-1.27714100	0.15922700	-0.13258200
C	1.27717700	0.15917000	0.13242300
C	0.00004800	0.87318700	-0.00021900
C	-2.39199300	-2.02839700	-0.47058500
H	-3.17847600	-2.08822100	-1.22623000
H	-2.84023900	-1.81367400	0.49526300
H	-1.90093300	-3.00247700	-0.41795100
C	-0.50124200	-1.39041000	-1.90449100
H	0.16829300	-2.20617100	-1.62190500
H	0.08438900	-0.53581200	-2.22901000
H	-1.11050100	-1.72646600	-2.74684100
C	-3.69332800	0.63216200	-0.30457400
H	-4.10061900	1.63943100	-0.40366900
H	-4.39833000	0.03138200	0.27358500
H	-3.58361000	0.20878300	-1.29849900
C	-2.35937600	1.70451000	1.46025500
H	-2.41195400	2.72459600	1.08078900
H	-1.44900300	1.60125000	2.04083300
H	-3.21813700	1.50732000	2.10397500
C	0.50076600	-1.39018400	1.90433900

Atom	x	y	z
H	-0.16875900	-2.20593400	1.62169500
H	-0.08488500	-0.53550100	2.22859900
H	1.10979400	-1.72617200	2.74688300
C	2.39180700	-2.02849200	0.47094800
H	3.17811500	-2.08828500	1.22677800
H	2.84028900	-1.81392000	-0.49482400
H	1.90068500	-3.00254100	0.41832200
C	2.35991000	1.70410900	-1.46044900
H	2.41248800	2.72425700	-1.08115300
H	1.44967500	1.60083300	-2.04123600
H	3.21881300	1.50672700	-2.10392200
C	3.69336600	0.63191900	0.30484100
H	3.58340100	0.20870700	1.29881000
H	4.10074300	1.63916000	0.40386000
H	4.39842300	0.03097400	-0.27308100
N	-1.38374400	-1.01722600	-0.80004100
N	-2.38799400	0.73613200	0.35691200
N	1.38356100	-1.01720400	0.80005400
N	2.38817800	0.73592100	-0.35692700
O	0.00004500	2.13720000	-0.00006200

Cartesians coordinates for the optimized geometry of $1^{\bullet+}$

(*in "acetonitrile", using the default polarizable continuum model*)

(E = -727.539188)

Atom	x	y	z
C	1.26928000	0.17753400	0.15455900
C	-1.26922600	0.17764100	-0.15458700
C	0.00006600	0.90290400	-0.00003600
C	2.34177500	-2.02047200	0.52659200
H	3.12298500	-2.07435600	1.28715100
H	2.79245400	-1.83303700	-0.44318700
H	1.82962800	-2.98338200	0.49331100
C	0.45119100	-1.33336000	1.93685400
H	-0.22296700	-2.14466000	1.65757500
H	-0.12500300	-0.46800400	2.24715900
H	1.05478100	-1.66391500	2.78465300
C	3.69649200	0.59297400	0.31885600
H	4.14669300	1.58494700	0.37810700
H	4.36941200	-0.05809200	-0.24232200
H	3.57396900	0.20916400	1.32698900
C	2.39779200	1.62854500	-1.49216700
H	2.57239100	2.65865100	-1.17970700
H	1.45462100	1.57853000	-2.02424300
H	3.20147600	1.31744300	-2.16196800
C	-0.45148900	-1.33320500	-1.93710600

Atom	x	y	z
H	0.22269300	-2.14452800	-1.65795800
H	0.12467100	-0.46786100	-2.24750100
H	-1.05523300	-1.66373000	-2.78480600
C	-2.34192400	-2.02025400	-0.52662500
H	-3.12323600	-2.07402300	-1.28708600
H	-2.79246000	-1.83284200	0.44322500
H	-1.82985100	-2.98320800	-0.49347000
C	-2.39761900	1.62843000	1.49245800
H	-2.57216900	2.65860400	1.18020200
H	-1.45445600	1.57826400	2.02452900
H	-3.20132200	1.31723400	2.16219500
C	-3.69642200	0.59319200	-0.31867600
H	-3.57397200	0.20951300	-1.32686700
H	-4.14661200	1.58518000	-0.37776600
H	-4.36931400	-0.05793800	0.24246100
N	1.34847300	-0.98718400	0.83439000
N	2.39266100	0.73063700	-0.33561500
N	-1.34858100	-0.98702500	-0.83448900
N	-2.39254600	0.73074400	0.33572900
O	0.00016000	2.17228500	-0.00019000

Table S1: computed geometric parameters of $\mathbf{1}^{2+}$ and $\mathbf{1}^{\bullet+}$ *(in vaccuo)*. Experimental values from single crystal X-ray diffraction study are in brackets.

	$\mathbf{1}^{2+}$	$\mathbf{1}^{\bullet+}$
Bond lengths (pm) [a,b]		
N1-C1	132.4 (132.1)	134.4
N2-C1	133.3 (132.3)	135.7
C1-C2	155.2 (153.7)	147.0
C2-O1	119.6 (120.0)	126.4
Angles (°)[a,b]		
N1-C1-N2	124.3 (125.4)	119.1
C1-C2-C1'	122.3(120.9)	121.8
Torsion (°)[a,b]		
N1-C1-C2-O1	36.3 (36.8)	30.6

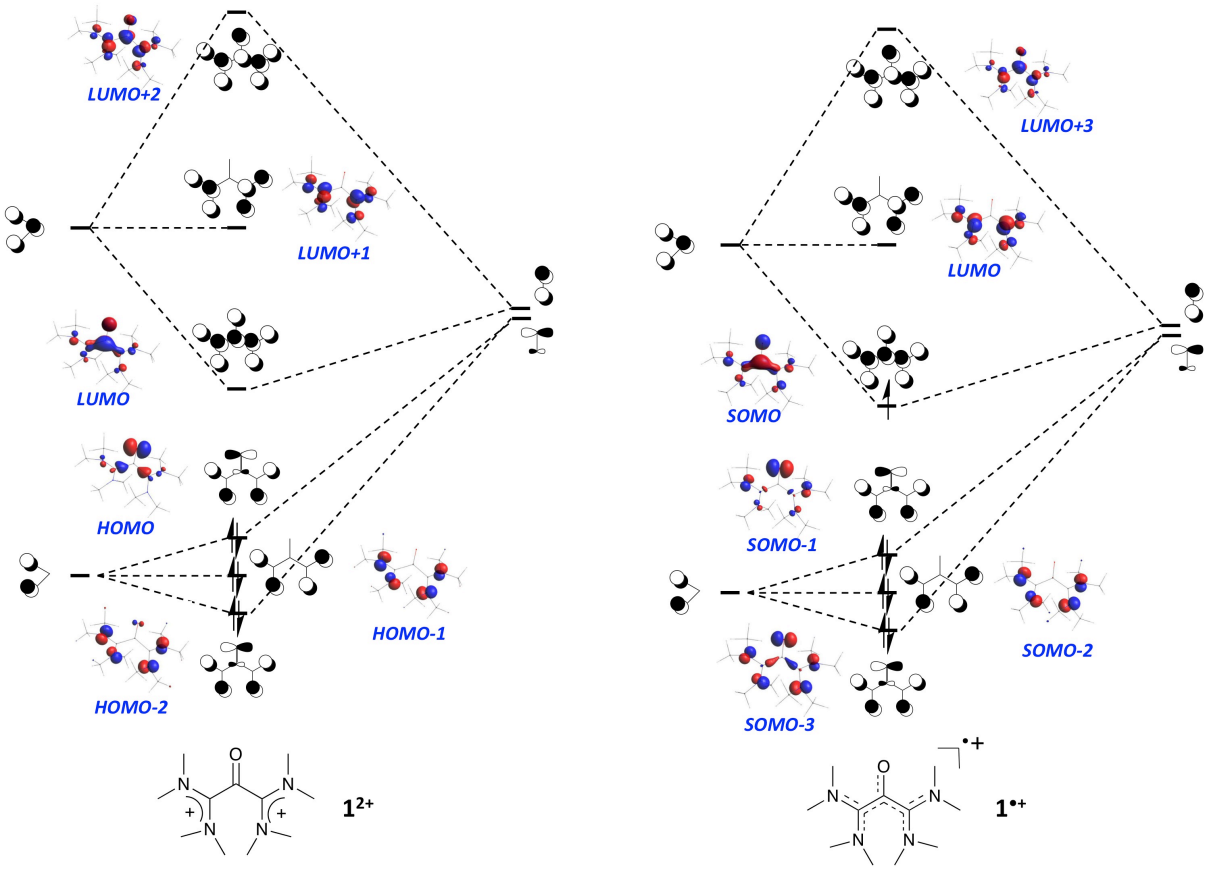


Figure S2: representation of relevant frontier π-molecular orbitals of $\mathbf{1}^{2+}$ (left) and $\mathbf{1}^{\bullet+}$ (right); qualitative construction from π* molecular orbitals of NCN and CO fragments.