Electronic Supplementary Information

Experimental and theoretical charge density assessments for the 4-perfluoropyridyl- and 4-perflurophenyl-1,2,3,5-dithiadiazolyl radicals

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Table S1 Refined parameters in the experimental and theoretical multipolar model for the NF-radical.

parameter	Experimental	Theoretical
Resolution cutoff 1.137 Å^{-1}	1	1
Hexadecapolar level on S atoms	1	1
Octupolar level on remaining non-H atoms	1	1
κ' for S	Fixed at average 1.114 from initial theoretical model	Refined freely for all sulphur atoms
κ' for F	Fixed at average 1.136 from initial theoretical model	Refined freely for all fluorine atoms
Anharmonicity of 3rd order for S atoms	1	-
Symmetry and equivalence constraints on some multipolar values	1	0
Kappa equivalence constraints	1	0

Table S2 Refined parameters in the experimental and theoretical multipolar model for the F-radical.

parameter	Experimental	Theoretical
Resolution cutoff 1.137Å^{-1}	1	1
Hexadecapolar level on S atoms	1	1
Octupolar level on remaining non-H atoms	1	1
κ' for S	Fixed at average 1.116 from initial theoretical model	Refined freely for all sulphur atoms

☐' for F	Fixed at average 1.130 from initial theoretical model	Refined freely for all fluorine atoms
Anharmonicity of 3rd order for S atoms	1	-
Symmetry and equivalence constraints on some multipolar values	1	0
Kappa equivalence constraints	1	0

Table S3 BCP properties for the intermolecular interactions within radical dimer of NF-radical. See Figure 5 for the BCPs locations.

NF-radical	Interaction	Experimental		Theoretical	
		☐(r) [eÅ^{-3}]	☐^{2}☐(r) [eÅ^{-5}]	☐(r) [eÅ^{-3}]	☐^{2}☐(r) [eÅ^{-5}]
Cp1	S1 … S2	0.166	1.12	0.156	1.11
Cp2	C1 … C1	0.035	0.40	-	-
Cp3	C6 … C6	0.055	0.59	0.053	0.58
Cp4	F1 … N1	-	-	0.076	1.44
Cp5	F4 … N2	-	-	0.078	1.46

Table S4 BCP properties for intermolecular interactions within radical dimer of F-radical. See Figure 5 for the BCPs locations.

F-radical	Interaction	Experimental		Theoretical	
		☐(r) [eÅ^{-3}]	☐^{2}☐(r) [eÅ^{-5}]	☐(r) [eÅ^{-3}]	☐^{2}☐(r) [eÅ^{-5}]
Cp1	S1 … S2	0.149	1.22	0.167	1.18
Cp2	F1 … N1	0.063	1.22	0.067	1.31
Cp3	F5 … N2	0.074	1.39	0.077	1.47
Cp4	C3 … C3	0.053	0.57	0.049	0.58
Cp5	F1 … C2	-	-	0.042	0.59

Table S5 Electron density ☐(r) [eÅ^{-3}] and laplacian, ☐^{2}☐(r) [eÅ^{-5}] in NF-radical for noncovalent interactions.

Interaction (ORTEP code)	Experimental		Theoretical	
	$\rho(r)$	$\nabla^2\rho(r)$	$\rho(r)$	$\nabla^2\rho(r)$
S2 ... N1 (56552)	0.035	0.39	0.035	0.38
N2 ... S1 (56552)	0.036	0.40	0.036	0.40
N3 ... S1 (54501)	0.049	0.55	0.055	0.59
N3 ... S2 (54501)	0.052	0.58	0.058	0.62
S2 ... F1 (56552)	0.040	0.60	0.039	0.59
F3 ... S2 (54501)	0.044	0.58	0.044	0.60
F4 ... S1 (56552)	0.054	0.83	0.051	0.80
F1 ... F3 (55452)	0.038	0.68	0.036	0.69
F2 ... F3 (55452)	0.045	0.84	0.045	0.85
F3 ... F3 (65751)	0.029	0.60	0.029	0.61
F3 ... F4 (65751)	0.050	1.05	0.050	1.06

Table S6 Electron density $\rho(r)$ [eÅ^{-3}] and laplacian, $\nabla^2\rho(r)$ [eÅ^{-5}] in F-radical for noncovalent interactions.

Interaction (ORTEP code)	Experimental		Theoretical	
	$\rho(r)$	$\nabla^2\rho(r)$	$\rho(r)$	$\nabla^2\rho(r)$
S2 ... N1 (56552)	0.056	0.57	0.064	0.66
N2 ... S1 (56552)	0.058	0.57	0.065	0.66
S1 ... F5 (56552)	0.036	0.58	0.039	0.59
S2 ... F5 (54504)	0.015	0.24	0.016	0.24
S2 ... F1 (56552)	0.033	0.61	0.037	0.60
F3 ... S1 (54501)	-	-	0.057	0.77
F3 ... S2 (54501)	0.057	0.79	0.067	0.86
F4 ... N2 (54504)	0.039	0.65	0.041	0.67
F1 ... F2 (65551)	0.023	0.47	0.022	0.47
F2 ... F2 (65551)	0.034	0.70	0.034	0.71
F3 ... F5 (54504)	0.012	0.23	0.012	0.23

F4 … F5 (54504)	0.036	0.75	0.036	0.75

Table S7 Electron density $\rho(r)$ [eÅ^{-3}] and laplacian, $\nabla^2\rho(r)$ [eÅ^{-5}] values for the covalent bonds in the dithiadiazolyl ring obtained from the final experimental and theoretical model.

	NF-radical				F-radical			
	Experimental		Theoretical		Experimental		Theoretical	
Bond	$\rho(r)$	$\nabla^2\rho(r)$	$\rho(r)$	$\nabla^2\rho(r)$	$\rho(r)$	$\nabla^2\rho(r)$	$\rho(r)$	$\nabla^2\rho(r)$
S1-S2	0.957	-2.42	0.937	-1.920	0.875	-1.02	0.914	-1.43
S1-N1	1.578	-8.21	1.505	-7.770	1.567	-4.42	1.463	-5.94
S2-N2	1.579	-8.24	1.507	-7.750	1.576	-4.54	1.471	-6.09
N1-C1	2.380	-21.36	2.324	-20.960	2.336	-21.92	2.292	-20.18
N2-C1	2.372	-21.03	2.317	-20.810	2.338	-22.03	2.295	-20.21

Table S8 Deformation density statistics on 3D grids

	NF-radical		F-radical	
	Experimental	Theoretical	Experimental	Theoretical
δ_{max}	0.933	1.060	0.894	1.084
δ_{min}	-1.360	-2.230	-1.071	-2.178
δ	1.7E-07	2.9E-07	1.4E-06	9.2E-07
$\langle|\delta|\rangle$	0.038	0.041	0.039	0.041
RMS	0.038	0.041	0.039	0.041
RMSD	**0.016**		**0.021**	
Correlation R	**0.925**		**0.868**	

Table S9 Interaction energies, E_{int}, and its components, E_{vdW} and $E_{SOMO-SOMO}$ [kJ/mol]

	Experimental / 6-31G**			Experimental / 6-311++G**		
Dimer	E_{int}	E_{vdW}	$E_{SOMO-SOMO}$	E_{int}	E_{vdW}	$E_{SOMO-SOMO}$
NF-radical	-46.8	32.6	-79.4	-47.2	34.5	-81.7
F-radical	-46.9	37.4	-84.3	-48.6	38.1	-86.7

Table S10 Electrostatic interaction energies [kJ/mol] for NF-radical.

Symmetry	Experimental	Theoretical
X ; Y-1 ; Z	-9.0	-23.0
X ; -Y ; Z-1/2	-9.7	-8.4
X ; -Y ; Z+1/2	-8.6	-7.5
X ; -Y+1 ; Z-1/2	-11.8	-19.1
X ; Y+1 ; Z	-9.3	-23.6
X ; -Y+1 ; Z+1/2	-11.4	-18.8
-X+1 ; Y-1 ; -Z+3/2	0.4	-4.3
-X+1 ; Y ; -Z+3/2	-76.3	-61.4
-X+1 ; -Y+1 ; -Z+1	-0.4	-3.0
-X+1 ; Y+1 ; -Z+3/2	0.5	-4.2
-X+1 ; -Y+1 ; -Z+2	-1.4	-6.5
-X+3/2 ; Y-1/2 ; -Z+3/2	-3.0	-0.8
-X+3/2 ; Y+1/2 ; -Z+3/2	-3.3	-0.6
-X+3/2 ; -Y+1/2 ; -Z+2	-21.1	-29.5
RMSD	**8.0**	
Correlation R	**0.927**	

Table S11 Electrostatic interaction energies [kJ/mol] for F-radical.

Symmetry	Experimental	Theoretical
X ; Y-1 ; Z	-23.9	-16.2
X ; -Y ; Z-1/2	-7.9	-8.1
X ; -Y ; Z+1/2	-7.3	-8.1
X ; -Y+1 ; Z-1/2	-24.7	-23.8
X ; Y+1 ; Z	-23.9	-15.8
X ; -Y+1 ; Z+1/2	-24.9	-24.2

-X+1 ; Y-1 ; -Z+1/2	-8.2	-2.4
-X+1 ; -Y ; -Z	7.6	1.6
-X+1 ; Y ; -Z+1/2	-26.4	-69.8
-X+1 ; -Y+1 ; -Z	-9.9	-5.2
-X+1 ; Y+1 ; -Z+1/2	-8.3	-2.5
-X+1 ; -Y+1 ; -Z+1	-2.3	-3.1
-X+1/2 ; -Y-1/2 ; -Z	5.2	0.7
-X+1/2 ; Y-1/2 ; -Z+1/2	-4.7	-3.2
-X+1/2 ; -Y+1/2 ; -Z	-30.5	-24.5
-X+1/2 ; Y+1/2 ; -Z+1/2	-4.4	-3.0
RMSD	**12**	
Correlation R	**0.729**	

Table S12 Dipole moments [D] for dimers as obtained from multipolar models and quantum calculations using DFT method with B97D functional and 6-311++G** basis set. The same experimental geometry was used.

Model	NF-radical	F-radical
Experimental multipolar model	1.68	20.23
Theoretical multipolar model	11.87	9.99
Quantum calculations	7.19	4.46

Table S13 AIM charges for NF-radical.

	Experimental		Theoretical	
atom	Q [e]	Volume [$Å^3$]	Q [e]	Volume [$Å^3$]
S1	0.449	24.516	0.614	24.192
S2	0.453	23.593	0.606	23.303
N1	-0.805	15.105	-0.934	15.473
N2	-0.805	14.061	-0.952	14.438
C1	0.773	7.237	0.803	7.017

C2	0.074	9.292	0.062	9.070
C3	0.539	8.024	0.524	8.046
C4	1.011	6.489	0.922	6.675
N3	-0.730	15.075	-0.928	15.530
C5	1.001	6.848	0.892	7.059
C6	0.530	8.180	0.501	8.266
F1	-0.654	15.158	-0.520	14.958
F2	-0.592	14.610	-0.529	14.454
F3	-0.585	14.416	-0.530	14.293
F4	-0.652	14.386	-0.528	14.202
Dithiadiazolyl-ring	**0.064**	84.513	**0.137**	84.423
6-membered ring	**-0.059**	112.479	**-0.134**	112.554
Total	**0.005**	196.991	**0.003**	196.978
RMSD	**0.113**	**0.258**		
Correlation *R*	**0.987**	**0.999**		

Table S14 AIM charges for F-radical.

atom	Experimental		Theoretical	
	Q [e]	Volume [Å^3]	Q [e]	Volume [Å^3]
S1	0.491	23.746	0.594	24.130
S2	0.496	23.349	0.616	23.621
N1	-0.757	13.870	-0.953	14.127
N2	-0.755	14.311	-0.941	14.502
C1	0.922	7.038	0.797	7.106
C2	0.270	8.686	0.054	9.368
C3	0.509	8.443	0.484	8.365
C4	0.516	8.195	0.470	8.258
C5	0.649	8.238	0.477	8.889

C6	0.524	8.092	0.515	8.018
C7	0.517	8.628	0.509	8.495
F1	-0.707	16.282	-0.520	15.772
F2	-0.663	16.334	-0.516	16.036
F4	-0.677	14.884	-0.524	14.537
F5	-0.709	16.950	-0.513	16.410
F3	-0.620	18.000	-0.544	17.512
Dithiadiazolyl-ring	**0.397**	82.315	**0.113**	83.486
6-membered ring	**-0.390**	132.732	**-0.108**	131.660
Total	**0.007**	215.047	**0.005**	215.145
RMSD	**0.141**	**0.375**		
Correlation R	**0.975**	**0.998**		

Table S15 Electrostatic Potential quantities computed at the Hirshfeld surface. The quantities: $V_{S,\max}$, $V_{S,\min}$, $\overline{V}_S^{\square}$, $\overline{V}_S^{\square}$, $\overline{V}_S$ and $\square$ are given in e/Å; $\square_{\square}^2$, $\square_{\square}^2$ and $\square_{\text{tot}}^2$ are in (e/Å)^2; $\square$ is dimensionless.

	NF-radical		F-radical	
Surface quantity	Experimental	Theoretical	Experimental	Theoretical
$V_{S,\max}$	0.1406	0.1929	0.2544	0.2038
$V_{S,\min}$	-0.0686	-0.1034	-0.0930	-0.0758
$\overline{V}_S^{\square}$	0.0326	0.0544	0.0836	0.0479
$\overline{V}_S^{\square}$	-0.0250	-0.0352	-0.0538	-0.0305
$\overline{V}_S$	0.0146	0.0165	0.0205	0.0151
$\square$	0.0268	0.0448	0.0699	0.0392
$\square_{\square}^2$	0.0005	0.0013	0.0021	0.0011
$\square_{\square}^2$	0.0003	0.0004	0.0007	0.0002
$\square_{\text{tot}}^2$	0.0008	0.0016	0.0028	0.0013

☐	0.2218	0.1695	0.1873	0.1427
RMSD	**0.0367**		**0.0452**	
Correlation *R*	**0.733**		**0.861**	

Table S16 Total atomic spins [au] for the NF-radical molecule in its crystal lattice obtained from periodic calculations using Crystal09 and the DFT method in UB3LYP\6-31G**. The symmetry related molecules have opposite spins, and total spin is summed to zero.

Atom	Spin
S1	0.147
S2	0.144
N1	0.127
N2	0.129
C1	-0.060
C2	0.010
C3	-0.008
C4	0.003
N3	-0.006
C5	0.004
C6	-0.008
F1	0.000
F2	0.000
F3	0.000
F4	0.000
Dithiadiazolyl ring	0.487
4-perfluoropyridyl ring	-0.005
Total	0.482

(a)   (b)
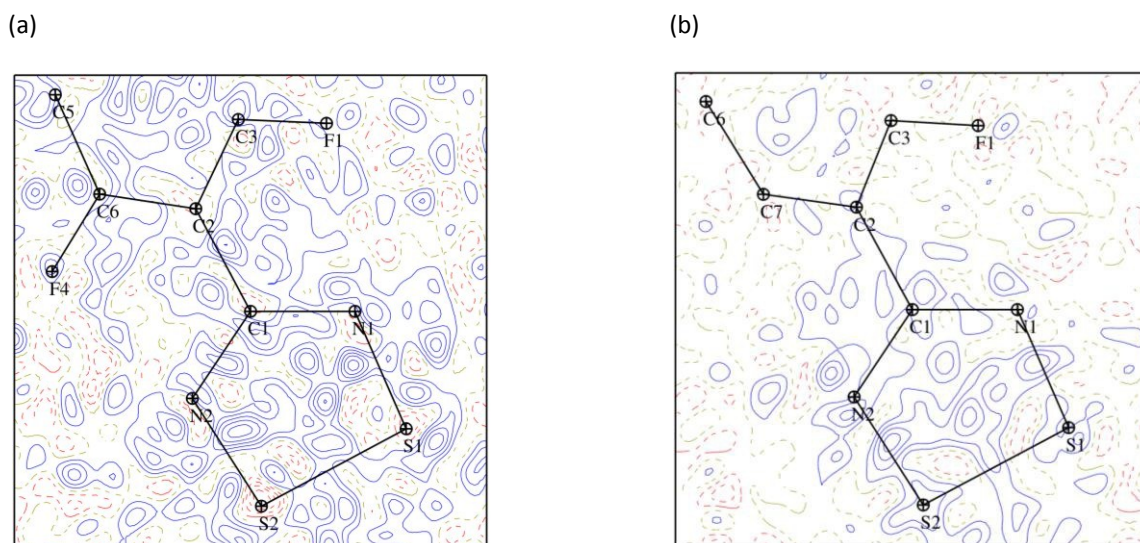
Figure S1 Residual density maps for the NF-radical (a) and F-radical (b) at the full resolution up to 1.137 Å^{-1}. The contour lines are displayed with step ±0.05 eÅ^{-3}. The maximum peak are equal +0.28 and +0.23 eÅ^{-3}, for NF-radical and F-radical, respectively. The deepest holes are equal -0.24 and -0.14 eÅ^{-3} for NF-radical and F-radical, respectively.
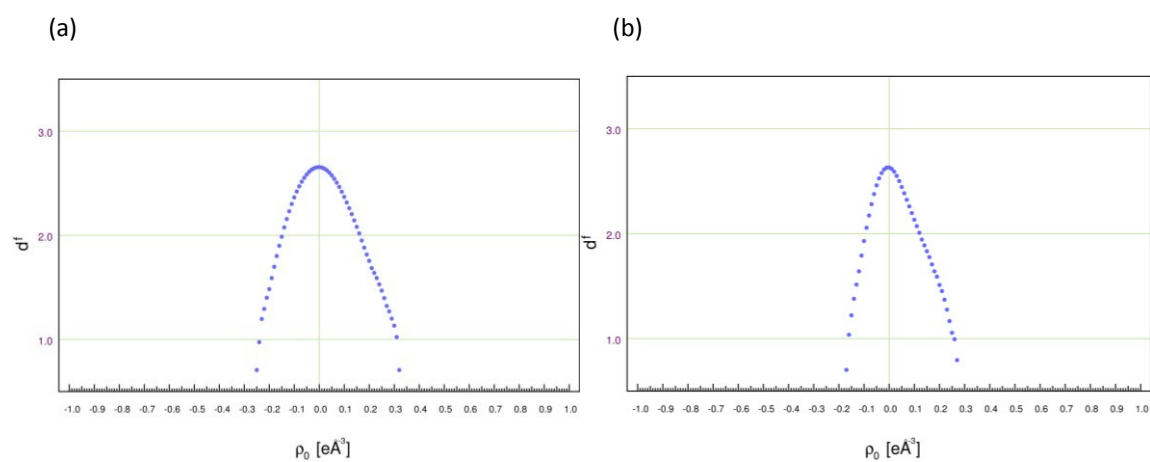
(a)   (b)

Figure S2 Fractal residual maps for the NF-radical (a) and F-radical (b).

(a)   (b)
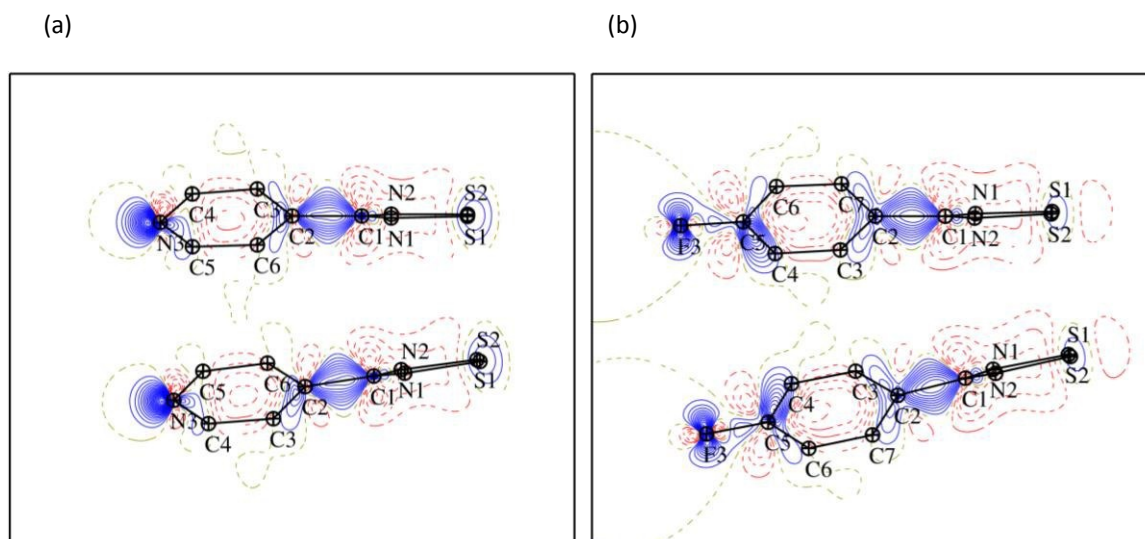
Figure S3 Deformation density maps in dimers of (a) NF-radical and (b) F-radical. Maps are shown in the plane of the C1 and the C2 atom of the first molecule and the C2 atom of the second molecule. Contour level: ± 0.05 eÅ^{-3}. Blue solid lines and red dashed lines denote positive and negative contours, respectively.
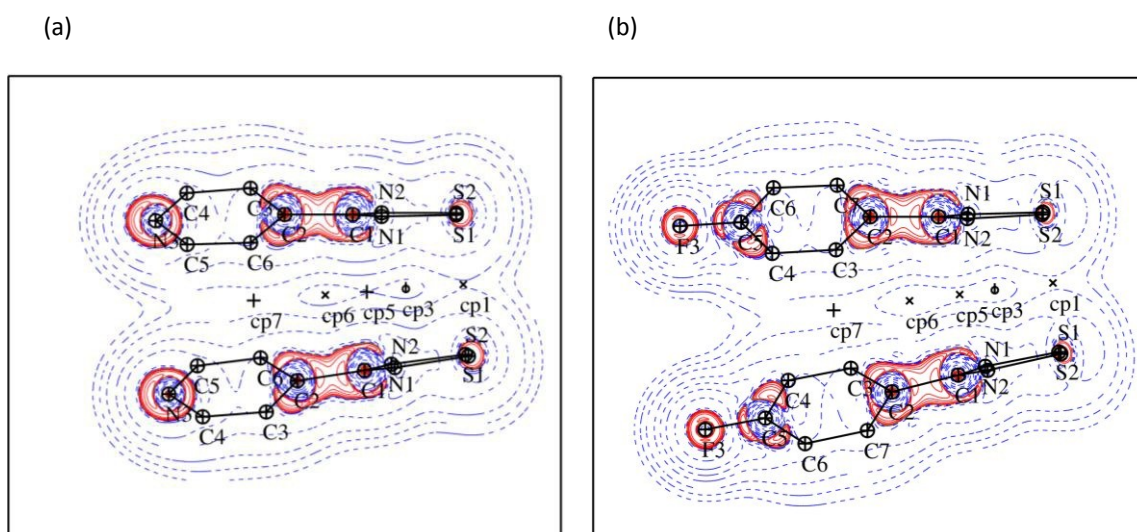
(a)   (b)

Figure S4 Laplacian maps in dimers (a) NF-radical and (b) F-radical. Maps are shown in the plane of the C1 and the C2 atom of the first molecule and the C2 atom of the second molecule. Blue (dashed) and red (solid) lines represent positive and negative values. Contours are drawn at $\pm 2^m \times 10^n$ e Å^{-5} (m = 1, 2, 3; n = -1, 0, 1, 2) levels. The '+', 'x' and ϕ symbols denote the bond, ring and the cage critical points, respectively.
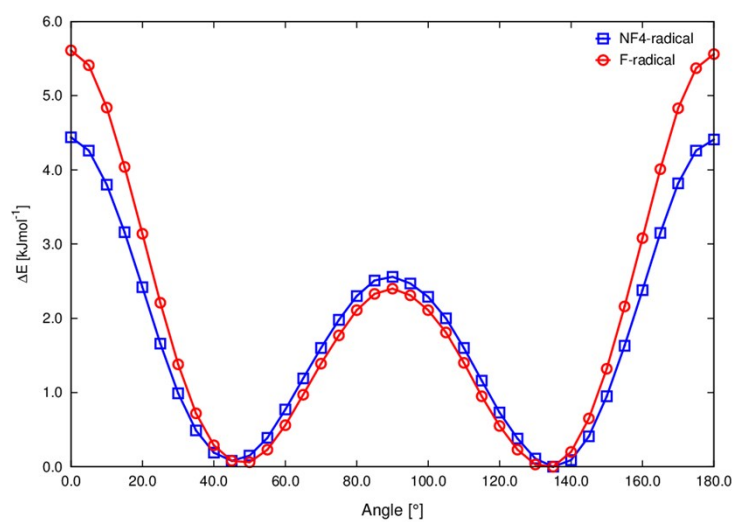
Figure S5 Relaxed potential energy scan around torsion angle between 5-membered ring and 6-membered ring for NF-radical and F-radical monomer. The DFT method was used with UB3LYP functional and 6-31G** basis set.