

*Electronic Supplementary Information*

**Synthesis of Porphyrin(2.1.2.1) Pd(II) Complexes Embedded  
with Various  $\pi$  Units and Their Singlet Oxygen Generation  
Capacity**

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*Dedicated to Prof. Karl M. Kadish on the occasion of his 80th birthday*

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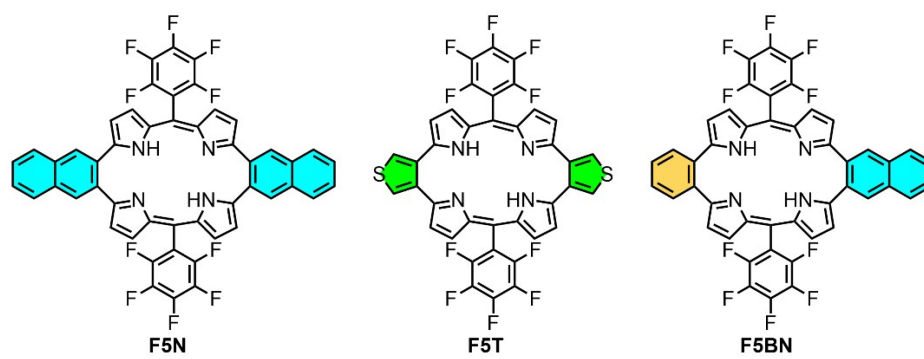
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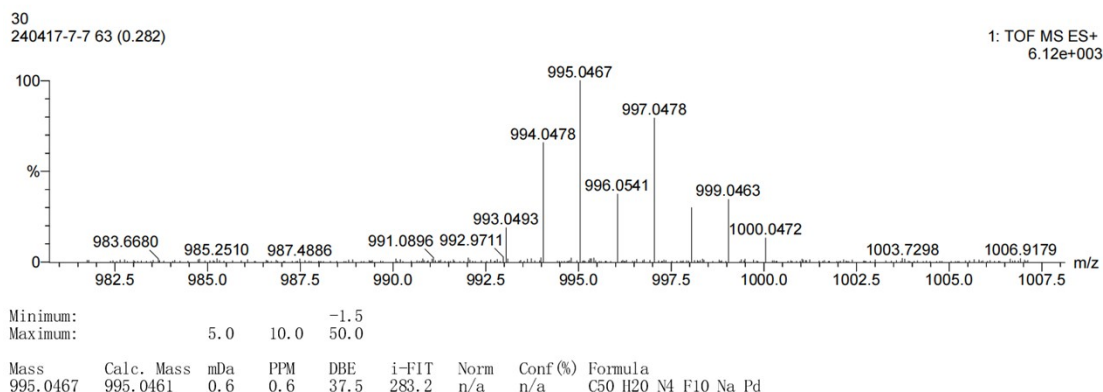
- 1, Supporting Figures
- 2, Cartesian Coordinates

## 1, Supporting Figures



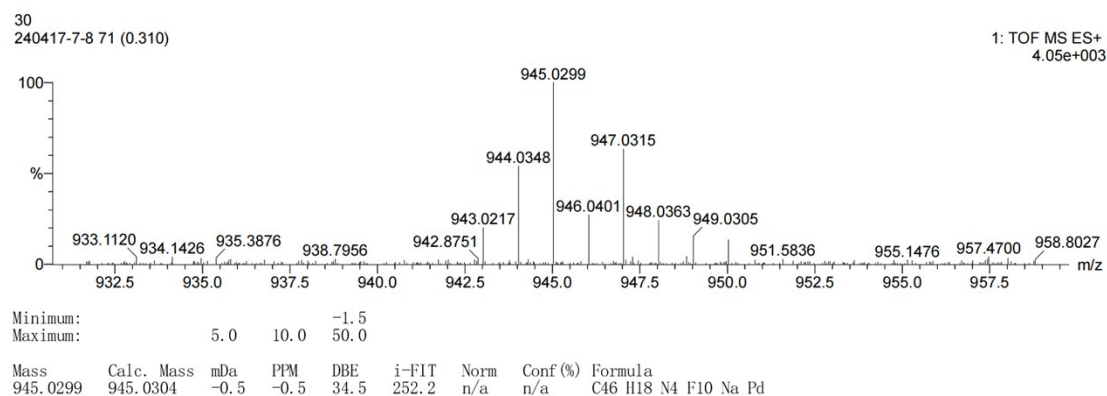
**Figure S1.** Molecular structure of **F5N**, **F5T** and **F5BN**.

Monoisotopic Mass, Even Electron Ions  
 2154 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)  
 Elements Used:  
 C: 50-50 H: 20-20 N: 0-100 O: 0-100 F: 10-10 Na: 0-1 Pd: 1-1

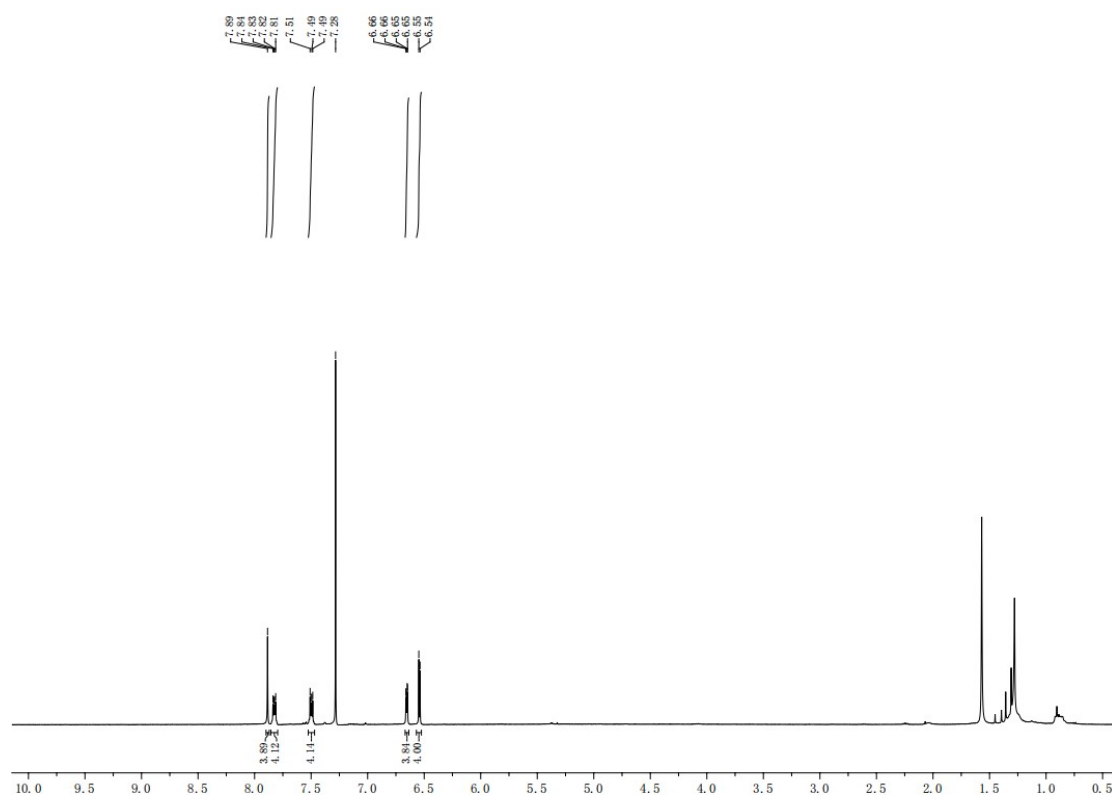


**Figure S2.** HR-ESI-MS spectrum of **F5NPd**.

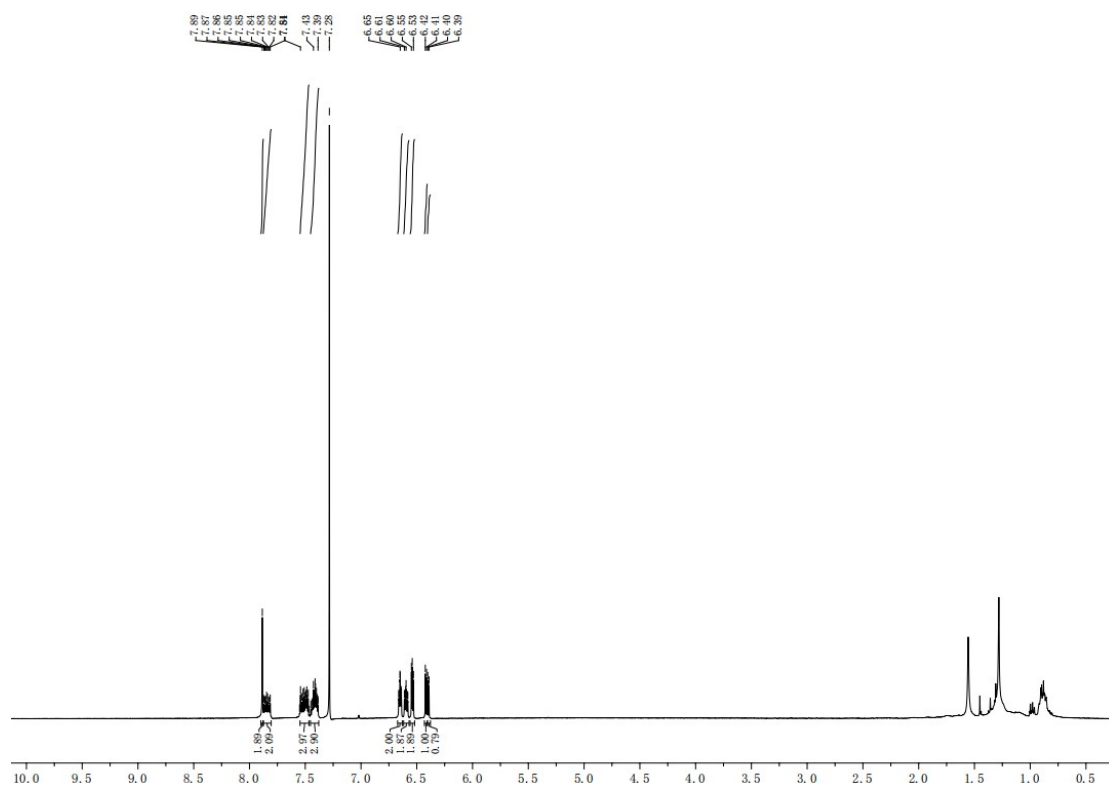
Monoisotopic Mass, Even Electron Ions  
 1853 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)  
 Elements Used:  
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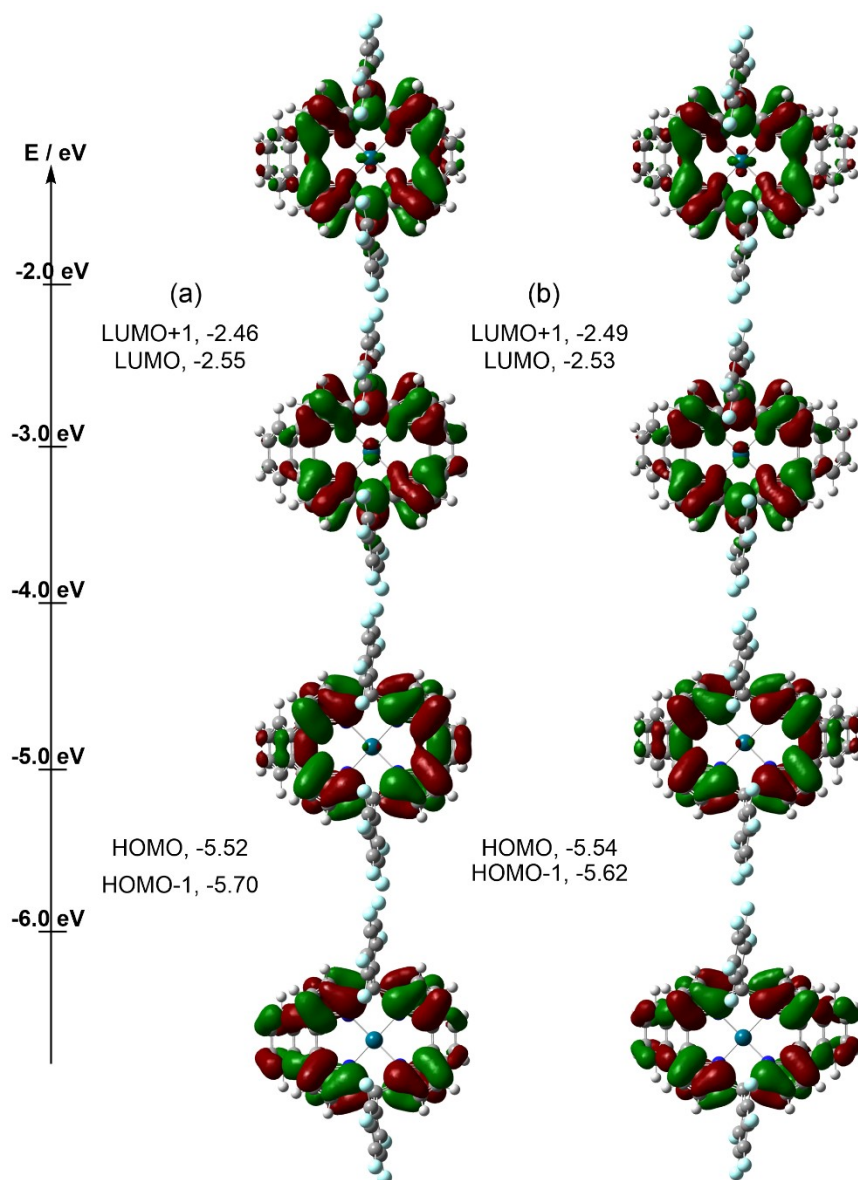
**Figure S3.** HR-ESI-MS spectrum of **F5BNPd**.



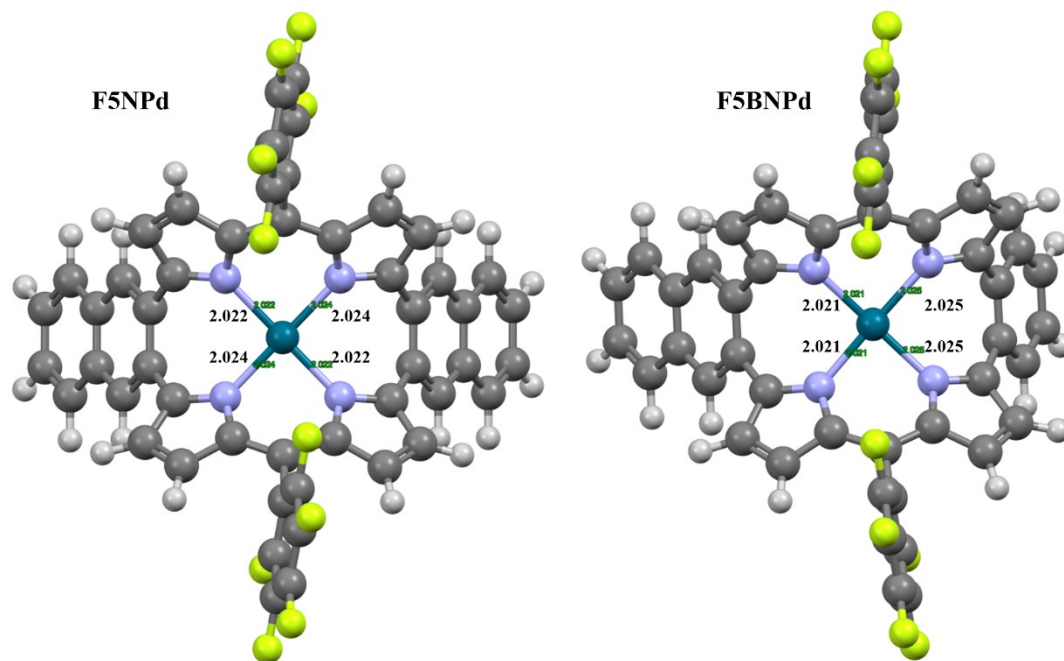
**Figure S4.**  $^1\text{H}$  NMR spectrum of **F5NPd** recorded at 298 K in  $\text{CDCl}_3$ .



**Figure S5.**  $^1\text{H}$  NMR spectrum of F5BNPd recorded at 298 K in  $\text{CDCl}_3$ .

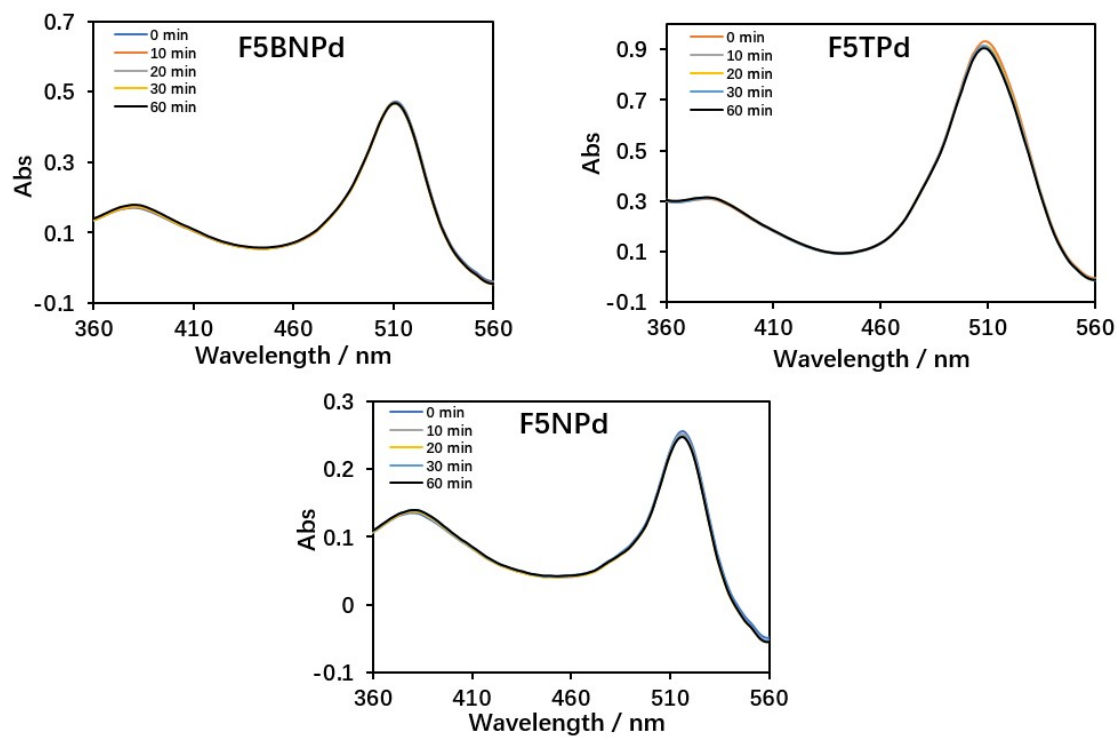


**Figure S6.** Frontier molecular orbital and energy levels of (a-b) **F5BNPd** and **F5NPd** calculated at the B3LYP/6-31G(d, p) (C, N, H, F) + SDD (Pd) basis set.

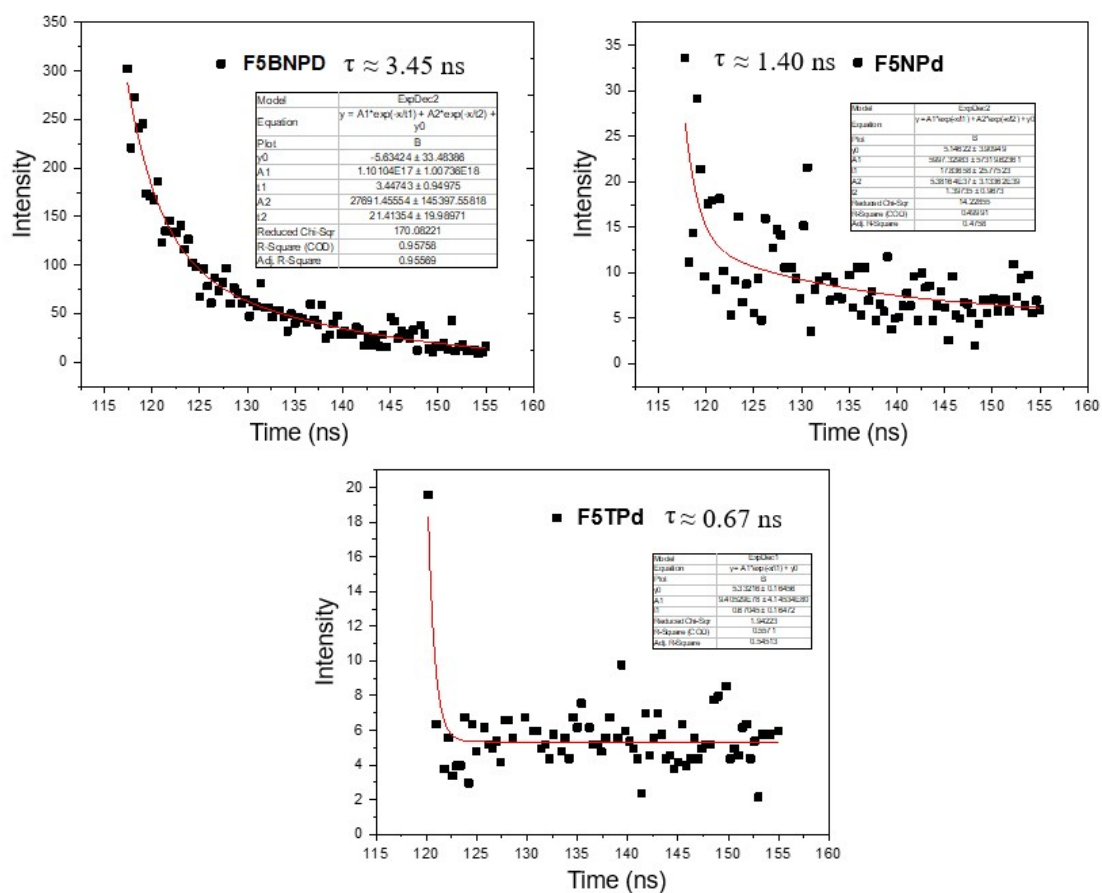


**Figure S7.** Optimized molecular structures and selected bond distances of **F5BNPd** and **F5NPd** calculated at the B3LYP/6-31G(d, p) (C, N, H, F) + SDD (Pd) basis set.





**Figure S8.** UV-vis absorption spectra of **F5BNPd**, **F5TPd**, and **F5NPd** under blue light for 1 hour.



**Figure S9.** Phosphorescence decay profiles of F5BNPd, F5TPd, and F5NPd in air saturated toluene. The line (in red) is a least-squares fit assuming a single exponential.

## 2, Cartesian Coordinates

**F5BNPd** at ground state

Total energy: E = -3105.81926327 a.u.

Pd	-0.00000200	0.54865300	0.66004600
N	-1.45399400	-0.25149500	1.82033900
N	-1.44925200	1.06440500	-0.65074500
N	1.44922700	1.06444900	-0.65076000
N	1.45404600	-0.25141500	1.82031800
C	-2.45853800	-1.01017000	1.23867500
C	-2.88534000	-0.84600300	-0.08222300
C	-2.45896700	0.16468000	-0.95034300
C	-1.52517800	2.06045500	-1.54173800
C	-2.58168400	1.81662200	-2.46315600
C	-3.14924400	0.61585900	-2.10988200
C	-0.71422300	3.28260400	-1.51742800
C	0.71413200	3.28262800	-1.51742900
C	1.52513000	2.06050700	-1.54174300
C	2.45897500	0.16475700	-0.95035500
C	2.88536100	-0.84593600	-0.08225500
C	2.45855500	-1.01013700	1.23863800
C	1.52121300	-0.44853700	3.14190300
C	2.56532000	-1.36494700	3.45129200
C	3.13054600	-1.74242500	2.25738600
C	0.70358700	0.24093800	4.14551600
C	-0.70354500	0.24086800	4.14554600
C	-1.52117200	-0.44859500	3.14193300
C	-2.56532300	-1.36495800	3.45132800
C	-3.13056700	-1.74241800	2.25742900
C	-1.38211000	0.85353300	5.20842900
C	-0.69618400	1.47330800	6.24394400
C	0.69621500	1.47339000	6.24390200
C	1.38214700	0.85368000	5.20835200
C	3.98141300	-1.72828000	-0.56871600
C	3.14924800	0.61597000	-2.10988400
C	2.58165500	1.81671700	-2.46315300
C	1.38694600	4.48771300	-1.58488400
C	0.71254500	5.72796400	-1.62820200
C	-0.71271900	5.72793900	-1.62820200
C	-1.38707700	4.48766500	-1.58488200
C	-3.98137900	-1.72836900	-0.56867000
C	-5.31015700	-1.52082500	-0.20441200
C	-6.32962500	-2.34127800	-0.67212500
C	-6.02401600	-3.39415700	-1.52657400
C	-4.70702400	-3.62142200	-1.90791000
C	-3.70255000	-2.78842200	-1.42930400
C	3.70263200	-2.78825200	-1.42946600
C	4.70713000	-3.62122700	-1.90806200
C	6.02409700	-3.39401800	-1.52660300
C	6.32966000	-2.34121700	-0.67204200

C	5.31016800	-1.52078700	-0.20433700
F	-2.45120600	-3.02858200	-1.80653700
F	-4.41786000	-4.62884500	-2.72358500
F	-6.99032400	-4.18234500	-1.97790300
F	-7.59027700	-2.12352800	-0.31307500
F	-5.63206300	-0.51583800	0.60486700
F	2.45131300	-3.02836000	-1.80681200
F	4.41801800	-4.62857900	-2.72384300
F	6.99042300	-4.18218700	-1.97792800
F	7.59028800	-2.12351700	-0.31287900
F	5.63203200	-0.51587200	0.60504600
C	-1.40153300	6.96544200	-1.67428800
C	-0.70712500	8.14932000	-1.71768300
C	0.70686700	8.14934400	-1.71768000
C	1.40131600	6.96549100	-1.67428400
H	-2.85233900	2.46837000	-3.28243700
H	-3.99098800	0.11937000	-2.57244900
H	2.82671100	-1.69472100	4.44741500
H	3.95532100	-2.42417400	2.10360000
H	-2.82671400	-1.69473100	4.44745100
H	-3.95537900	-2.42412400	2.10364800
H	-2.46826000	0.84502600	5.20318500
H	-1.24685700	1.95287600	7.04768400
H	1.24688000	1.95302800	7.04760600
H	2.46829700	0.84527000	5.20305000
H	3.99100800	0.11950600	-2.57245100
H	2.85230200	2.46848400	-3.28242200
H	2.47396400	4.48268300	-1.59299500
H	-2.47409500	4.48259900	-1.59299000
H	-2.48851400	6.96140000	-1.67286700
H	-1.24308100	9.09336900	-1.75132100
H	1.24279000	9.09341300	-1.75131500
H	2.48829700	6.96148600	-1.67286000

**F5NPd** at ground state

Total energy: E = -3259.28658319 a.u.

Pd	0.00000000	0.49270100	0.00000000
N	-1.46747400	0.32591800	1.38348800
N	-1.43404100	0.32963700	-1.41598900
N	1.46747300	0.32592400	-1.38348900
N	1.43404100	0.32963200	1.41598800
C	-2.46073700	-0.62696500	1.21674600
C	-2.87537700	-1.10001000	-0.03149800
C	-2.44398700	-0.60658100	-1.26744300
C	-1.50131300	0.79351900	-2.66981800
C	-2.55396300	0.14839300	-3.37713500
C	-3.12643400	-0.74916100	-2.50800500
C	-0.67815200	1.87565600	-3.21992000
C	0.75029100	1.86192700	-3.21021000
C	1.54689600	0.76781800	-2.64392300
C	2.46073700	-0.62695900	-1.21675200
C	2.87537700	-1.10000800	0.03149100
C	2.44398800	-0.60658500	1.26743800
C	1.50131300	0.79350900	2.66981900
C	2.55396400	0.14838100	3.37713300
C	3.12643500	-0.74917000	2.50799900
C	0.67815100	1.87564400	3.21992600
C	-0.75029300	1.86191400	3.21021500
C	-1.54689700	0.76780700	2.64392300
C	-2.58643800	0.08848200	3.33928700
C	-3.13768000	-0.80765900	2.45568500
C	-1.43747300	2.88193800	3.83997600
C	-0.77778200	3.95830100	4.47341700
C	0.64737500	3.97278100	4.48211600
C	1.33652500	2.90983300	3.85764400
C	3.95993100	-2.11936500	0.05931500
C	3.13767700	-0.80764900	-2.45569200
C	2.58643400	0.08849500	-3.33928900
C	1.43747100	2.88195300	-3.83996600
C	0.77778000	3.95831800	-4.47340200
C	-0.64737700	3.97279800	-4.48210000
C	-1.33652600	2.90984700	-3.85763400
C	-3.95993000	-2.11936600	-0.05932500
C	-5.29384700	-1.78459500	0.16410200
C	-6.30089800	-2.74162400	0.12455200
C	-5.97703500	-4.06569000	-0.14705500
C	-4.65460300	-4.42605100	-0.37683200
C	-3.66295300	-3.45312800	-0.33367300
C	3.66295600	-3.45312600	0.33366700
C	4.65460600	-4.42604800	0.37682600
C	5.97703700	-4.06568700	0.14704600
C	6.30089900	-2.74162200	-0.12456500
C	5.29384700	-1.78459300	-0.16411500
F	-2.40599800	-3.82419300	-0.55337300

F	-4.34838000	-5.69249500	-0.63420300
F	-6.93101800	-4.98597100	-0.18654000
F	-7.56693900	-2.39948900	0.33852600
F	-5.63322000	-0.52377500	0.41645100
F	2.40600100	-3.82419100	0.55337000
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F	7.56694000	-2.39948700	-0.33854100
F	5.63322000	-0.52377400	-0.41646600
C	1.32129600	5.04547300	5.11730400
C	0.61285100	6.05792200	5.71612500
C	-0.80101200	6.04349000	5.70750500
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C	-1.32129800	5.04549300	-5.11728400
C	-0.61285300	6.05794400	-5.71610100
C	0.80101000	6.04351200	-5.70748200
C	1.48122400	5.01684500	-5.10014100
H	-2.81747900	0.34121200	-4.40800100
H	-3.96661500	-1.40462800	-2.69145600
H	2.81748100	0.34119600	4.40800000
H	3.96661600	-1.40463800	2.69144700
H	-2.85450000	0.25807800	4.37305100
H	-3.95626500	-1.49126300	2.63281600
H	-2.52439600	2.86213500	3.83852800
H	2.42353500	2.91195000	3.87016200
H	3.95626100	-1.49125300	-2.63282700
H	2.85449500	0.25809400	-4.37305300
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