

Supporting Information:

Simulation of metal-organic framework self-assembly

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S.1 Simulation methods

We applied the flexible all-atom model for the 4,4'-bpy ligand model with the exception that the bond-stretching degrees of freedom were constrained to the equilibrium bond lengths with the LINCS bond constraint algorithm.¹ The general AMBER force field² was used for the intermolecular and intramolecular interactions. For the ligand atomic charges, we used restrained electrostatic potential (RESP) charges,³ obtained using *ab initio* molecular orbital (MO) calculations with the B3LYP/6-31G(d) level in the Gaussian03 program.⁴ For the metal atom nonbonded interaction parameters, we started from the values in the universal force field (UFF)⁵ and the van der Waals bond length was scaled to reproduce the metal-N_{bpy} distance from the XRD study. The cationic dummy atom (CaDA) method⁶ was applied for the metal-ligand coordination interaction. The atomic charge of the metal cation evenly transferred to the dummy atoms that were attached coplanarly to the metal for the Pd(II) and octahedrally for the Ru(II). The metal-dummy atom distance was set to 0.09 nm as in the original CaDA paper.⁶ Comparison between the binding energy of metal with ligand calculated using the present force field and *ab initio* MO calculations are presented in the next section of this supporting informations.

As in our previous studies,^{7,8} we applied a coarse-grained (implicit) solvent model that combines the three methods, Langevin dynamics (LD),⁹ the generalized reaction field method¹⁰ and Weeks-Chandler-Andersen (WCA) type short-range repulsive potentials,¹¹ but we did not include any atomistic solvents, which had been used in some of our previous systems.^{7,8} Langevin dynamics, which adds a friction and random force to the conventional molecular dynamics, was applied to account for the dynamic (e.g. heat bath) effects of the solvent molecules. In the generalized reaction field method, the relative dielectric constant beyond the distance parameter for the complete screening can be separately specified as the far field value from the near-field value. Similar to the electrostatic screening, van der Waals interactions between the ligands are also screened by the solvation to effectively be short-range repulsive WCA potential which truncates at the repulsive part of the common Lennard-Jones potential and shifted. We did not include counter anions (e.g., NO₃⁻) as in our previous studies. In reality, MOF self-assembly take much longer time than that in our model (and the time conventional MD simulations can reach), as the coordination of ligands (bpys) requires time for the dissociation of solvents, or anions from metal ions. Then, our model (without real solvents and anions) overestimates the rate of their (metal ions) coordination to the ligands. Because of the overestimation, our model is surely very poor model for evaluation of the accurate coordination rate. At the same time, however, this overestimation effectively accelerates the rate of the metal's coordination to the ligands and enables our model to realize the MOF self-assembly within the available computational time. To study the MOF self-assembly, we should take into account the elements that play important roles in the self-assembly process, but we think it is not equal to use as more realistic model as possible. Currently, We do not have evidences that show the dissociation process of solvents or anions from metal ions are playing such active roles. Regarding this, we did not include the real solvents and anions in our current model as we aimed to propose the "minimum" model that realize the MOF self-assembly.

Trajectories were produced using the molecular dynamics program GROMACS (version 4.5.7)¹² with a modified nonbonded interaction routine to employ the WCA potential described above. For LD time

integration, we used the leapfrog stochastic dynamics integrator¹³ and LINCS bond constraint¹ with a 4 fs time step due to the stability of the LINCS algorithm and the hydrogen mass repartitioning (to increase the mass of hydrogen atoms while maintaining the total molecular mass).¹⁴ The simulation temperature was maintained at 293 K by coupling to a stochastic thermostat with the time constant $\tau_t=0.1$ ps *via* LD. The LD friction coefficient for each atom was specified as the GROMACS default value (*i.e.*, mass/τ_t).

Charge group-based, twin-range 0.65 nm van der Waals and 1.4 nm electrostatic cutoff distances¹⁵ were applied to the non-bonded interactions. The setting of the former short value (0.65 nm) is due to the utilization of the short-ranged WCA potential. In the generalized reaction field method, the far- and near-field relative dielectric constants were set to 47.0 and 2.5, respectively for the Pd(II) in DMSO system. The latter value (2.5) was applied because this value was the optimum value found in our previous studies.^{7,8} For the Ru(II) in nitromethane system, the far-field relative dielectric constant was set to 36.2. We found that the near-field relative dielectric constant of 1.75 was the optimum value for the regular MOF self-assembly.

S.2 Metal-ligand binding energy

Comparison of the calculated metal-ligand binding energy between the present force-field and *ab initio* MO calculations are summarized in the following table S1. The binding energy was obtained as the dissociation energy of a pyridine (py) from Pd(II)(py)₄ complex. The MP2/6-31G* level optimized geometry of Pd(II)(py)₄ was used for calculating the metal-ligand binding energy. The DGDZVP basis set¹⁶ was used for Pd.

The binding energy value with the present force-field calculation was middle between standard HF and high-level MP2 methods and we think it would be sufficient level for the present study.

Table S1: Calculated metal-ligand binding energy (kcal/mol)

	HF	MP2	present force-field
			-52.8
6-31G*	-49.65	-61.18	
6-311G*	-49.20	-61.26	
6-311G**	-49.10	-61.16	
cc-pVDZ	-48.79	-60.61	
aug-cc-pVDZ	-48.41	-65.05	

S.3 Bonding rates and density of the unbound pyridine rings

Fig. S1 shows Time evolution of the bonding rate (black line) and the number density of the unbound pyridine rings (red lines) in the self-assembly process of the [Pd(II)(4,4'-bpy)₂] system. Until $t=0.4 \mu\text{s}$, the coordination bonding rates were steeply decreased to zero depending on the density of the unbound pyridine rings. After $t=0.4 \mu\text{s}$, the bonding rates raised again by forced increase of the density of the unbound pyridine rings with the box shrinkage. The bonding rates closed to zero again at $t=0.8 \mu\text{s}$ since the number of coordination bonds closed to the full-bonding limit as shown in Fig. 3.

S.4 Topology file

The GROMACS molecular topology file for the 4,4'-bpy ligand and CaDA metal models with the atomic charge assignments that aided in reproducing the simulation in this study are presented in the last part of this documents. The topology file for the ligands was created using the program “acpype”¹⁷ as the interface for the automatic atom type and the bond type perception program “antechamber”.¹⁸

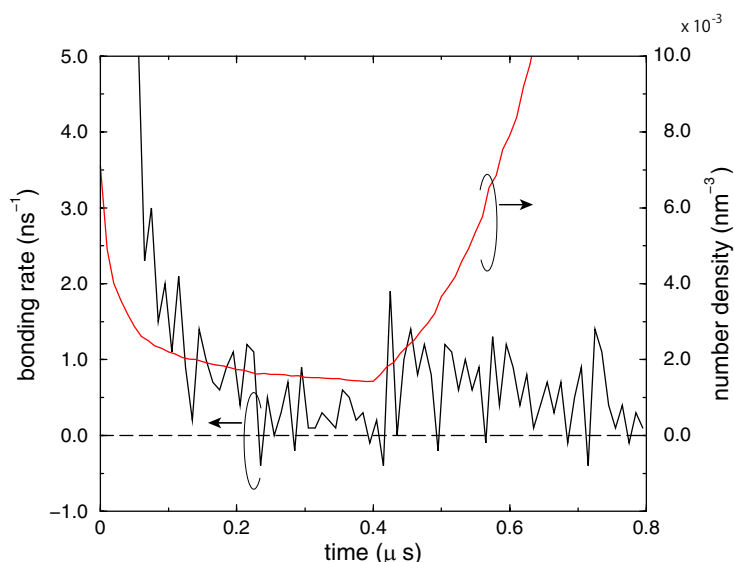


Figure S1: Time evolution of the bonding rate (black line) and the number density of the unbound pyridine rings (red lines) in the self-assembly process of the $[\text{Pd}(\text{II})(4,4'\text{-bpy})_2]$ system (shown in Fig. 3).

References

- 1 B. Hess, H. Bekker, H. J. C. Berendsen and J. G. E. M. Fraaije, *J. Comput. Chem.*, 1997, **18**, 1463
- 2 J. Wang, R. M. Wolf, J. W. Caldwell, P. A. Kollman and D. A. Case, *J. Comput. Chem.*, 2004, **25**, 1157
- 3 C. I. Bayly, P. Cieplak, W. Cornell and P. A. Kollman, *J. Chem. Phys.*, 1993, **97**, 10269
- 4 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, 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, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian03, Revision C.02*, Gaussian, Inc., Wallingford CT, 2004
- 5 A. K. Rappé, C. J. Casewit, K. Colwell, W. Goddard III and W. Skiff, *J. Am. Chem. Soc.*, 1992, **114**, 10024–10035
- 6 Y. Pang, *J. Mol. Model.*, 1999, **5**, 196–202
- 7 M. Yoneya, T. Yamaguchi, S. Sato and M. Fujita, *J. Am. Chem. Soc.*, 2012, **134**, 14401–14407
- 8 M. Yoneya, S. Tsuzuki, T. Yamaguchi, S. Sato and M. Fujita, *ACS nano*, 2014, **8**, 1290–1296
- 9 S. Yun-yu, W. Lu and W. Van Gunsteren, *Mol. Simul.*, 1988, **1**, 369–383
- 10 I. Tironi, R. Sperb, P. Smith and W. van Gunsteren, *J. Chem. Phys.*, 1995, **102**, 5451
- 11 J. Weeks, D. Chandler and H. Andersen, *J. Chem. Phys.*, 1971, **54**, 5237
- 12 B. Hess, C. Kutzner, D. Van Der Spoel and E. Lindahl, *J. Chem. Theory Comput.*, 2008, **4**, 435–447

- 13 W. van Gunsteren and H. Berendsen, *Mol. Simul.*, 1988, **1**, 173–185
- 14 K. A. Feenstra, B. Hess and H. J. Berendsen, *J. Comput. Chem.*, 1999, **20**, 786–798
- 15 E. Lindahl, B. Hess and D. van der Spoel, *J. Mol. Model.*, 2001, **7**, 306
- 16 N. Godbout, D. R. Salahub, J. Andzelm and E. Wimmer, *Canadian Journal of Chemistry*, 1992, **70**, 560–571
- 17 A. W. S. da Silva and W. F. Vranken, *BMC Res. Notes*, 2012, **5**, 367
- 18 J. Wang, W. Wang, P. Kollman and D. Case, *J. Mol. Graphics Model.*, 2006, **25**, 247–260

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; Supporting Information
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; Simulation of metal-organic framework self-assembly
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; author's names:
; Makoto Yoneya, Seiji Tsuzuki and Masaru Aoyagi
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;

[ defaults ]
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Ru6 76.90800 0.000 A 3.1676e-01 0.23430 ; x 1.2
DMY 4.03200 0.000 A 0.0 0.0
#else
Pd4 106.40000 0.000 A 2.5827e-01 0.20083 ; UFF orig.
Ru6 101.10000 0.000 A 2.6397e-01 0.23430 ; UFF orig.
DMY 0.00000 0.000 A 0.0 0.0
#endif

; name mass charge ptype sigma epsilon Amb
nb 0.00000 0.00000 A 3.25000e-01 7.11280e-01 ; 1.82 0.1700
ca 0.00000 0.00000 A 3.39967e-01 3.59824e-01 ; 1.91 0.0860
cp 0.00000 0.00000 A 3.39967e-01 3.59824e-01 ; 1.91 0.0860
h4 0.00000 0.00000 A 2.51055e-01 6.27600e-02 ; 1.41 0.0150
ha 0.00000 0.00000 A 2.59964e-01 6.27600e-02 ; 1.46 0.0150

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bpy-aa 3

[ atoms ]
; nr type resi res atom cgnr charge mass
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2 ca 1 MOL C1 1 0.416148 8.98600 ; qtot -0.184
3 ca 1 MOL C2 2 -0.455985 8.98600 ; qtot -0.640
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2 ca 1 MOL C1 1 0.416148 12.01000 ; qtot -0.184
3 ca 1 MOL C2 2 -0.455985 12.01000 ; qtot -0.640
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#ifdef HEAVY_H
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6 ca 1 MOL C5 1 0.416148 8.98600 ; qtot -0.377
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6 ca 1 MOL C5 1 0.416148 12.01000 ; qtot -0.377
#endif
7 cp 1 MOL C6 3 0.303354 12.01000 ; qtot -0.073
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8 ca 1 MOL C7 3 -0.455985 8.98600 ; qtot -0.529
9 ca 1 MOL C8 4 0.416148 8.98600 ; qtot -0.113
#else
8 ca 1 MOL C7 3 -0.455985 12.01000 ; qtot -0.529
9 ca 1 MOL C8 4 0.416148 12.01000 ; qtot -0.113
#endif
10 nb 1 MOL N2 4 -0.600350 14.01000 ; qtot -0.714
#ifdef HEAVY_H
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14 ha 1 MOL H2 2 0.161663 4.03200 ; qtot -0.565
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```

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16 h4 1 MOL H4 1 0.026672 1.00800 ; qtot -0.377
17 ha 1 MOL H5 3 0.161663 1.00800 ; qtot -0.215
18 h4 1 MOL H6 4 0.026672 1.00800 ; qtot -0.188
19 h4 1 MOL H7 4 0.026672 1.00800 ; qtot -0.162
20 ha 1 MOL H8 3 0.161663 1.00800 ; qtot 0.000
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```

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2 13 1 1.0880e-01 2.8694e+05 ; C1 - H1
3 4 1 1.3950e-01 3.9003e+05 ; C2 - C3
3 14 1 1.0870e-01 2.8811e+05 ; C2 - H2
4 5 1 1.3950e-01 3.9003e+05 ; C3 - C4
4 7 1 1.4900e-01 2.8995e+05 ; C3 - C6
5 6 1 1.3870e-01 4.0033e+05 ; C4 - C5
5 15 1 1.0870e-01 2.8811e+05 ; C4 - H3
6 16 1 1.0880e-01 2.8694e+05 ; C5 - H4
7 8 1 1.3950e-01 3.9003e+05 ; C6 - C7
7 12 1 1.3950e-01 3.9003e+05 ; C6 - C10
8 9 1 1.3870e-01 4.0033e+05 ; C7 - C8
8 17 1 1.0870e-01 2.8811e+05 ; C7 - H5
9 10 1 1.3420e-01 4.0426e+05 ; C8 - N2
9 18 1 1.0880e-01 2.8694e+05 ; C8 - H6
10 11 1 1.3420e-01 4.0426e+05 ; N2 - C9
11 12 1 1.3870e-01 4.0033e+05 ; C9 - C10
11 19 1 1.0880e-01 2.8694e+05 ; C9 - H7
12 20 1 1.0870e-01 2.8811e+05 ; C10 - H8

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1 14 1 ; N1 - H2
1 15 1 ; N1 - H3
2 5 1 ; C1 - C4
2 7 1 ; C1 - C6
2 16 1 ; C1 - H4
3 8 1 ; C2 - C7
3 12 1 ; C2 - C10
3 15 1 ; C2 - H3
4 9 1 ; C3 - C8
4 11 1 ; C3 - C9
4 13 1 ; C3 - H1
4 16 1 ; C3 - H4
4 17 1 ; C3 - H5
4 20 1 ; C3 - H8
5 8 1 ; C4 - C7
5 12 1 ; C4 - C10
5 14 1 ; C4 - H2
6 3 1 ; C5 - C2
6 7 1 ; C5 - C6
6 13 1 ; C5 - H1
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7 15 1 ; C6 - H3
7 18 1 ; C6 - H6
7 19 1 ; C6 - H7
8 11 1 ; C7 - C9
8 20 1 ; C7 - H8
9 12 1 ; C8 - C10
9 19 1 ; C8 - H7
10 17 1 ; N2 - H5
10 20 1 ; N2 - H8
11 18 1 ; C9 - H6
12 17 1 ; C10 - H5
13 14 1 ; H1 - H2
15 16 1 ; H3 - H4
17 18 1 ; H5 - H6
19 20 1 ; H7 - H8

```

```

[ angles ]
; ai aj ak funct theta cth
1 2 3 1 1.2263e+02 5.7907e+02 ; N1 - C1 - C2
1 2 13 1 1.1594e+02 4.3346e+02 ; N1 - C1 - H1
1 6 5 1 1.2263e+02 5.7907e+02 ; N1 - C5 - C4
1 6 16 1 1.1594e+02 4.3346e+02 ; N1 - C5 - H4
2 1 6 1 1.1586e+02 5.7404e+02 ; C1 - N1 - C5
2 3 4 1 1.1907e+02 5.6233e+02 ; C1 - C2 - C3
2 3 14 1 1.2001e+02 4.0585e+02 ; C1 - C2 - H2
3 2 13 1 1.2109e+02 4.0334e+02 ; C2 - C1 - H1
3 4 5 1 1.1875e+02 5.6149e+02 ; C2 - C3 - C4

```

```

3 4 7 1 1.2701e+02 5.2384e+02 ; C2 - C3 - C6
4 3 14 1 1.2108e+02 4.0166e+02 ; C3 - C2 - H2
4 5 6 1 1.1907e+02 5.6233e+02 ; C3 - C4 - C5
4 5 15 1 1.2108e+02 4.0166e+02 ; C3 - C4 - H3
4 7 8 1 1.2701e+02 5.2384e+02 ; C3 - C6 - C7
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5 6 16 1 1.2109e+02 4.0334e+02 ; C4 - C5 - H4
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8 7 12 1 1.1875e+02 5.6149e+02 ; C7 - C6 - C10
8 9 10 1 1.2263e+02 5.7907e+02 ; C7 - C8 - N2
8 9 18 1 1.2109e+02 4.0334e+02 ; C7 - C8 - H6
9 8 17 1 1.2001e+02 4.0585e+02 ; C8 - C7 - H5
9 10 11 1 1.1586e+02 5.7404e+02 ; C8 - N2 - C9
10 9 18 1 1.1594e+02 4.3346e+02 ; N2 - C8 - H6
10 11 12 1 1.2263e+02 5.7907e+02 ; N2 - C9 - C10
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```

[dihedrals] ; propers

; treated as RBs in GROMACS to use combine multiple AMBER torsions per quartet

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1 2 3 14 3 30.33400 0.00000 -30.33400 0.00000 0.00000 0.00000 ; N1- C1- C2- H2
1 6 5 4 3 30.33400 0.00000 -30.33400 0.00000 0.00000 0.00000 ; N1- C5- C4- C3
1 6 5 15 3 30.33400 0.00000 -30.33400 0.00000 0.00000 0.00000 ; N1- C5- C4- H3
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2 3 4 5 3 30.33400 0.00000 -30.33400 0.00000 0.00000 0.00000 ; C1- C2- C3- C4
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3 4 5 6 3 30.33400 0.00000 -30.33400 0.00000 0.00000 0.00000 ; C2- C3- C4- C5
3 4 5 15 3 30.33400 0.00000 -30.33400 0.00000 0.00000 0.00000 ; C2- C3- C4- H3
3 4 7 8 3 8.36800 0.00000 -8.36800 0.00000 0.00000 0.00000 ; C2- C3- C6- C7
3 4 7 12 3 8.36800 0.00000 -8.36800 0.00000 0.00000 0.00000 ; C2- C3- C6- C10
4 3 2 13 3 30.33400 0.00000 -30.33400 0.00000 0.00000 0.00000 ; C3- C2- C1- H1
4 5 6 16 3 30.33400 0.00000 -30.33400 0.00000 0.00000 0.00000 ; C3- C4- C5- H4
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5 4 3 14 3 30.33400 0.00000 -30.33400 0.00000 0.00000 0.00000 ; C4- C3- C2- H2
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8 7 12 20 3 30.33400 0.00000 -30.33400 0.00000 0.00000 0.00000 ; C7- C6- C10- H8
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9 8 7 12 3 30.33400 0.00000 -30.33400 0.00000 0.00000 0.00000 ; C8- C7- C6- C10
9 10 11 12 3 40.16640 0.00000 -40.16640 0.00000 0.00000 0.00000 ; C8- N2- C9- C10
9 10 11 19 3 40.16640 0.00000 -40.16640 0.00000 0.00000 0.00000 ; C8- N2- C9- H7
10 9 8 17 3 30.33400 0.00000 -30.33400 0.00000 0.00000 0.00000 ; N2- C8- C7- H5
10 11 12 20 3 30.33400 0.00000 -30.33400 0.00000 0.00000 0.00000 ; N2- C9- C10- H8
11 10 9 18 3 40.16640 0.00000 -40.16640 0.00000 0.00000 0.00000 ; C9- N2- C8- H6
12 7 8 17 3 30.33400 0.00000 -30.33400 0.00000 0.00000 0.00000 ; C10- C6- C7- H5
13 2 3 14 3 30.33400 0.00000 -30.33400 0.00000 0.00000 0.00000 ; H1- C1- C2- H2
15 5 6 16 3 30.33400 0.00000 -30.33400 0.00000 0.00000 0.00000 ; H3- C4- C5- H4
17 8 9 18 3 30.33400 0.00000 -30.33400 0.00000 0.00000 0.00000 ; H5- C7- C8- H6
19 11 12 20 3 30.33400 0.00000 -30.33400 0.00000 0.00000 0.00000 ; H7- C9- C10- H8

```

[dihedrals] ; impropers

; treated as propers in GROMACS to use correct AMBER analytical function

```

; i j k l func phase kd pn
1 2 13 3 1 180.00 4.60240 2 ; N1- C1- H1- C2
1 6 16 5 1 180.00 4.60240 2 ; N1- C5- H4- C4
2 4 3 14 1 180.00 4.60240 2 ; C1- C3- C2- H2
3 5 4 7 1 180.00 4.60240 2 ; C2- C4- C3- C6
6 4 5 15 1 180.00 4.60240 2 ; C5- C3- C4- H3
8 12 7 4 1 180.00 4.60240 2 ; C7- C10- C6- C3
8 18 9 10 1 180.00 4.60240 2 ; C7- H6- C8- N2
9 7 8 17 1 180.00 4.60240 2 ; C8- C6- C7- H5
11 7 12 20 1 180.00 4.60240 2 ; C9- C6- C10- H8
12 19 11 10 1 180.00 4.60240 2 ; C10- H7- C9- N2

```

```

; end of itp

#include "pd4p2.itp"
[ moleculetype ]
; Name          nrexcl
pd4p2          3

[ atoms ]
; nr      type  resnr  residue  atom  cgnr  charge  mass
  1      Pd4    1     PAT     Pd    1     0.0
#ifdef NEUTRALIZE
  2      DMY    1     CAT     D     1     0.0
  3      DMY    1     CAT     D     1     0.0
  4      DMY    1     CAT     D     1     0.0
  5      DMY    1     CAT     D     1     0.0
#else
  2      DMY    1     CAT     D     1     0.5
  3      DMY    1     CAT     D     1     0.5
  4      DMY    1     CAT     D     1     0.5
  5      DMY    1     CAT     D     1     0.5
#endif

[ bonds ]
; ai  aj  funct  r  k
  1  2  1  0.9000e-01  2.2604e+05
  1  3  1  0.9000e-01  2.2604e+05
  1  4  1  0.9000e-01  2.2604e+05
  1  5  1  0.9000e-01  2.2604e+05

[ angles ]
; ai  aj  ak  funct  theta  cth
  2  1  3  1  0.9000e+02  2.3023e+02
  2  1  5  1  0.9000e+02  2.3023e+02
  4  1  3  1  0.9000e+02  2.3023e+02
  4  1  5  1  0.9000e+02  2.3023e+02
  4  1  2  1  1.8000e+02  2.3023e+02
  5  1  3  1  1.8000e+02  2.3023e+02

[ dihedrals ]
; ai  aj  ak  al  funct  c0, c1
  1  2  5  3  2  0.0 167.36
  1  3  2  4  2  0.0 167.36
  1  4  3  5  2  0.0 167.36
  1  5  4  2  2  0.0 167.36

; end of itp

#include "ru6p2.itp"
[ moleculetype ]
; Name          nrexcl
ru6p2          3

[ atoms ]
; nr      type  resnr  residue  atom  cgnr  charge  mass
  1      Ru6    1     CAT     Ru    1     0.0
#ifdef NEUTRALIZE
  2      DMY    1     CAT     D     1     0.0
  3      DMY    1     CAT     D     1     0.0
  4      DMY    1     CAT     D     1     0.0
  5      DMY    1     CAT     D     1     0.0
  6      DMY    1     CAT     D     1     0.0
  7      DMY    1     CAT     D     1     0.0
#else
  2      DMY    1     CAT     D     1     0.33334
  3      DMY    1     CAT     D     1     0.33334
  4      DMY    1     CAT     D     1     0.33334
  5      DMY    1     CAT     D     1     0.33334
  6      DMY    1     CAT     D     1     0.33334
  7      DMY    1     CAT     D     1     0.33334
#endif

[ bonds ]
; ai  aj  funct  r  k
  1  2  1  0.9000e-01  2.2604e+05
  1  3  1  0.9000e-01  2.2604e+05
  1  4  1  0.9000e-01  2.2604e+05
  1  5  1  0.9000e-01  2.2604e+05
  1  6  1  0.9000e-01  2.2604e+05
  1  7  1  0.9000e-01  2.2604e+05

[ angles ]
; ai  aj  ak  funct  theta  cth
  2  1  3  1  0.9000e+02  2.3023e+02
  2  1  5  1  0.9000e+02  2.3023e+02
  4  1  3  1  0.9000e+02  2.3023e+02

```


4	1	5	1	0.9000e+02	2.3023e+02
4	1	2	1	1.8000e+02	2.3023e+02
5	1	3	1	1.8000e+02	2.3023e+02
6	1	2	1	0.9000e+02	2.3023e+02
6	1	3	1	0.9000e+02	2.3023e+02
6	1	4	1	0.9000e+02	2.3023e+02
6	1	5	1	0.9000e+02	2.3023e+02
7	1	2	1	0.9000e+02	2.3023e+02
7	1	3	1	0.9000e+02	2.3023e+02
7	1	4	1	0.9000e+02	2.3023e+02
7	1	5	1	0.9000e+02	2.3023e+02
7	1	6	1	1.8000e+02	2.3023e+02

[dihedrals]

```
; ai  aj  ak  al  funct  c0,  c1
  1   2   5   3    2    0.0 167.36
  1   3   2   4    2    0.0 167.36
  1   4   3   5    2    0.0 167.36
  1   5   4   2    2    0.0 167.36
  1   2   7   6    2    0.0 167.36
  1   6   2   4    2    0.0 167.36
  1   4   6   7    2    0.0 167.36
  1   7   4   2    2    0.0 167.36
; end of itp
```

[system]

```
bpy-Pd4
;bpy-Ru6
```

[molecules]

```
; Compound      nmols
bpy-aa           768
pd4p2            384
;ru6p2           256
```