Electronic supplementary information

Structural characterization of metal-metal bonded polymer $[Ru(L)(CO)_2]_n$ (L= 2,2'-bipyridine) in the solid state using high-resolution NMR and DFT chemical shift calculations

Guillaume Gerbaud,[*,a,†] ***Jean-Marie Mouesca,***[*,a] ***Sabine Hediger,***[a] ***Sylvie Chardon-Noblat,***[b] ***Frédéric Lafolet,***[b] ***Alain Deronzier,***[b] ***and Michel Bardet***[a]

[a] CEA, INAC, SCIB (UMR-E3 CEA/UJF, FRE 3200 CEA/CNRS), F-38054 Grenoble, France

[b] Université Joseph Fourier, Département de Chimie Moléculaire (CNRS, UMR-5250), Institut de Chimie Moléculaire de Grenoble (FR-2607), BP 53, F-38041 Grenoble Cedex 9, France

[‡] Present address: CNRS – UPR 9036, Laboratoire de Bioénergétique et Ingénierie des Protéines, Campus Joseph Aiguier, F-13402 Marseille Cedex 20, France

AUTHOR EMAIL ADDRESS: ggerbaud@ifr88.cnrs-mrs.fr, jean-marie.mouesca@cea.fr

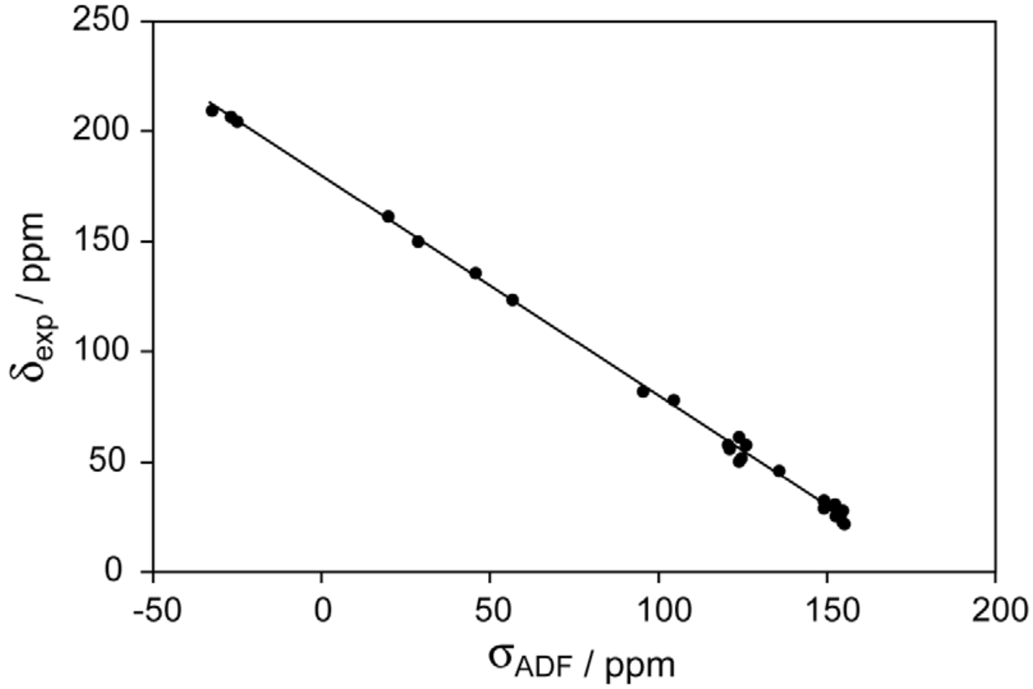

Figure S1. Plot of the experimental chemical shifts $\{\delta_{exp}\}$ as a function of computed screening constants $\{\sigma_{ADF}\}$ for a series of organic compounds (see Table S1 for a precise list). The best linear correlation between both quantities is found to be $\delta_{exp} \approx -0.9975 \times \sigma_{ADF} + 179.4$ ($R^2 = 0.9982$ and rms = 2.2 ppm). The rms value is defined as $(\Sigma_i^n (\delta_{ADF(i)} - \delta_{exp(i)})^2/n)^{1/2}$.

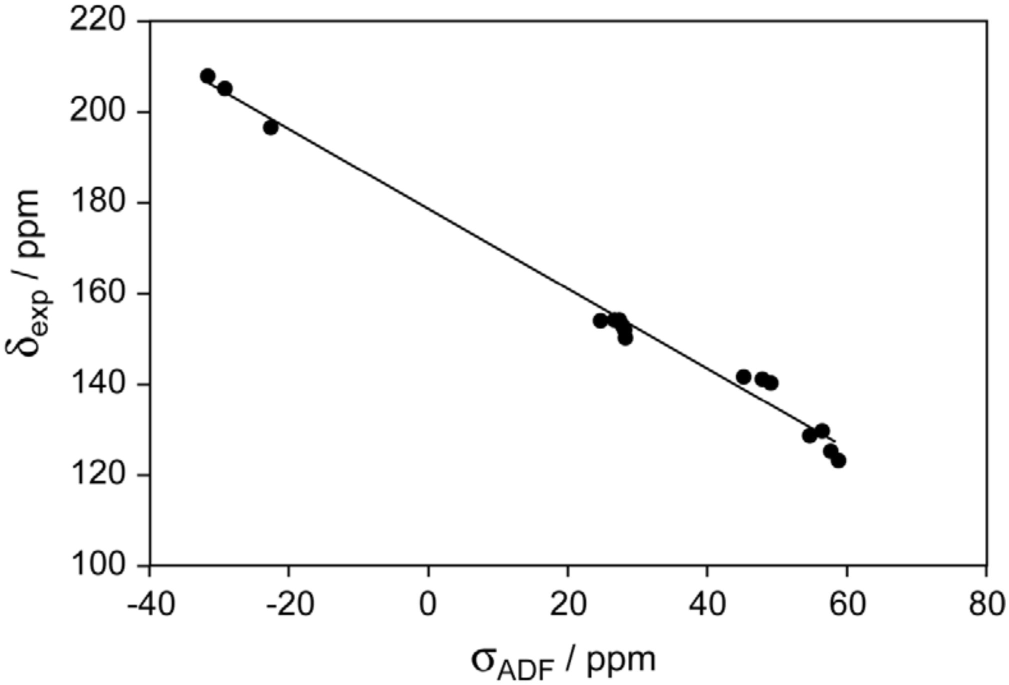

Figure S2. Common plot of the experimental NMR chemical shifts as a function of the corresponding computed (relativistic) shielding constants for both monomer $[Ru^{II}(bpy)(CO)_2(Cl)_2]$ and dimer $[Ru^{I}(bpy)(CO)_2(Cl)]_2$. The best linear correlation is found to be $\delta_{exp} \approx -0.8790 \times \sigma_{ADF} + 178.29$ ($R^2 = 0.9899$ and rms = 2.5 ppm). The rms value is defined as $(\Sigma_i^n (\delta_{ADF(i)} - \delta_{exp(i)})^2/n)^{1/2}$.

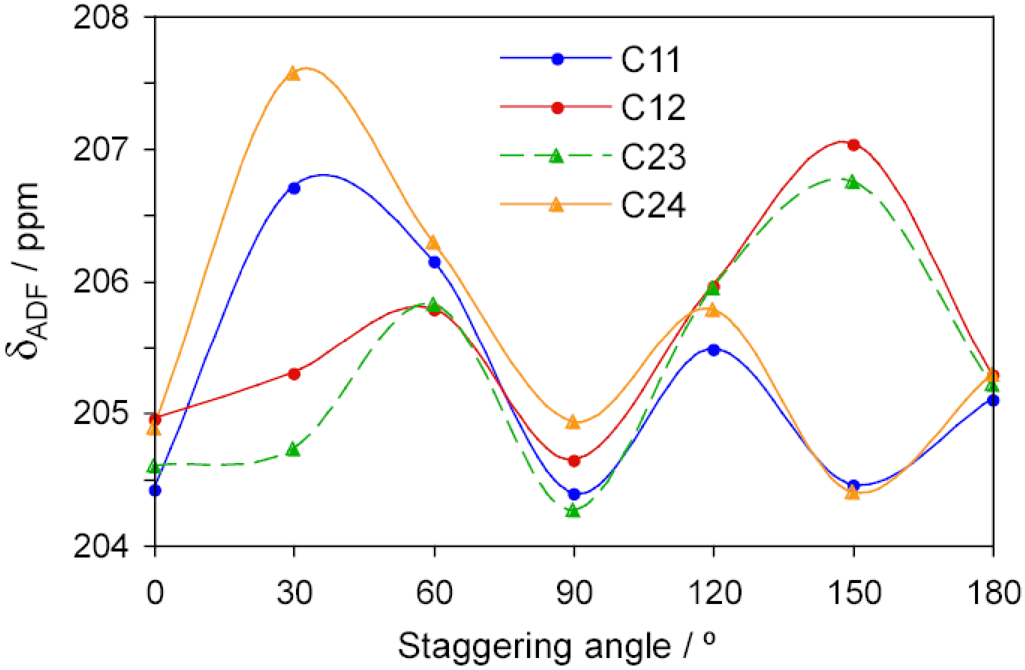

Figure S3. Predicted (ADF) chemical shifts for the four carbonyl nuclei of the dimer as a function of the (bipyridine-bipyridine) staggering angle. The corresponding computed data are reported in Table S3.

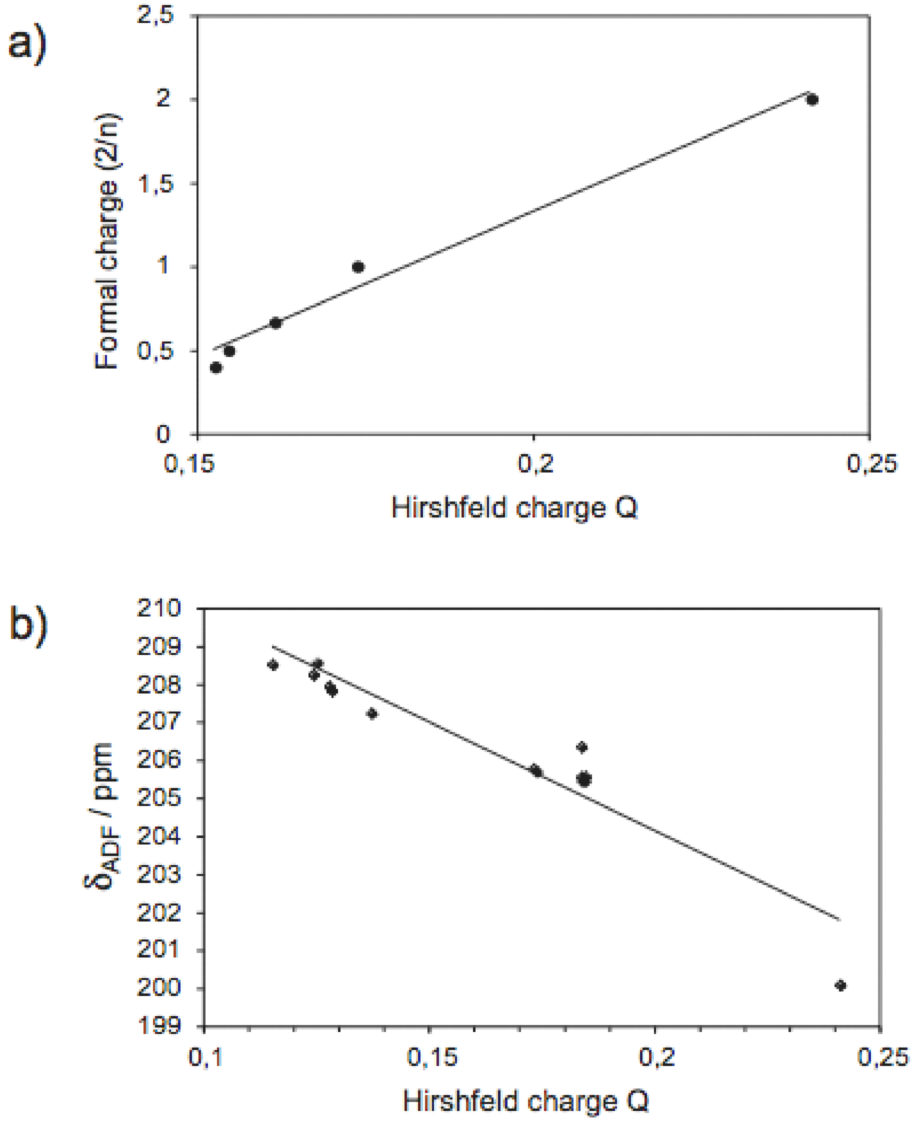

Figure S4. a) Formal charges (2/n) as a function of Hirshfeld charges (averaged over all Ru atoms within each of the five systems). For a wire (2/n→0), one would expect a (average) Hirshfeld charge of 2.1553 / 17.348 = 0.124.

b) Computed carbonyl chemical shifts $\{\delta_{ADF}\}$ as a function of the Ru Hirshfeld charge for the whole series of model systems, from the monomer to the pentamer (n=1-5). For each Ru site both carbonyl chemical shifts have been averaged. Best linear correlation gives a R^2 of 0.8985.

Tables S1. Experimental chemical shifts and corresponding computed shielding constants in ppm for a series of organic molecules : pyridine C_5H_5N (#1), 2,2'-bipyridine $(C_5H_4N)_2$ (#2), 4,4'-dimethyl-2,2'-bipyridine $(C_5H_3CH_3N)_2$ (#3), acetone $CH_3(C{=}O)CH_3$ (#4), ketones $CH_3(C{=}O)C{\equiv}CH$ (#5), $C_6H_{11}(C{=}O)CH_3$ (#6) and aldehyde $C_6H_{11}(C{=}O)H$ (#7).

Notice that, for molecule #3, the *trans* configuration (methyl groups on opposite positions) is found to be more stable than the *syn* configuration by 31.9 kJ/mol. We therefore report computed data only for the *trans* dimethyl molecule.

The experimental data for #1, #4-7 are extracted from E. Pretsch *et al.*[1] Those of #2-3 have been measured for this paper (present work). Computed chemical shifts $\{\delta_i\}$ are derived from $\delta_i = -0.9975 \times \sigma_{ADF} + 179.4$ (see main text and Figure S1).

#1	**Pyridine**		
C_i	δ_{exp}	σ_i	δ_i
2	149.8	28.66	150.8
3	123.6	56.58	123.0
4	135.7	45.77	133.8

#2	**2,2'-bipyridine**		
C_i	δ_{exp}	σ_i	δ_i
2	154.7	22.40	157.0
3	124.0*	61.21	118.4
4	135.7	45.80	133.7
5	120.6*	57.85	121.7
6	149.0	28.69	150.8

(*)We chose the best match between theory and experiment in case of ambiguous experimental assignments (positions 3 and 5).

Tables S1 continued.

#3	**4,4'-dimethyl-2,2'-bipyridine**		
C_i	δ_{exp}	σ_i	δ_i
2	155.1	21.80	157.6
3	126.0*	57.75	123.7
4	149.2	31.96	147.5
5	121.0*	55.90	121.8
6	149.2	32.27	147.2
CH_3	19.8	161.36	18.7

(*)We chose the best match between theory and experiment in case of ambiguous experimental assignments (positions 3 and 5).

#4	**Acetone $CH_3(C=O)CH_3$**		
C_i	δ_{exp}	σ_i	δ_i
1 (C=O)	206.7	-26.88	206.1
2	30.7	152.30	27.7

#5	**Ketone $CH_3(C=O)C{\equiv}CH$**		
C_i	δ_{exp}	σ_i	δ_i
2	81.9	95.42	84.3
3	78.1	104.56	75.2

#6	**Ketone $C_6H_{11}(C=O)CH_3$**		
C_i	δ_{exp}	σ_i	δ_i
1 (C=0)	209.4	-32.42	211.6
2 (CH_3)	27.6	154.70	25.3
3	51.5	124.59	55.3
4	29.0	152.62	27.4

5	26.6	153.07	26.9
6	26.3	152.91	27.1

Tables S1 continued.

#7	**Aldehyde $C_6H_{11}(C{=}O)H$**		
C_i	δ_{exp}	σ_i	δ_i
1 (C=0)	204.5	-24.92	204.2
2	50.1	123.99	55.9
3	26.1	154.08	25.9
4	25.2	153.43	26.5
5	25.2	152.54	27.4

Table S2. Bonding energies (eV) and relative energies (kJ/mol) for the $[Ru^{I}(bpy)(CO)_2(Cl)]_2$ dimer. Energies are reported relative to the minimum bonding energy: -351.611 eV (for 139°). A higher local minimum has been found at 46° (relative energy: 12.1 kJ/mol).

Angle (°)	Energies (eV)	Relative energies (kJ/mol)(a)
0	-351.294	30.6
30	-351.409	19.5
46	-351.485	12.1
60	-351.483	12.4
90	-351.395	20.8
120	-351.543	6.6
139	-351.611	0.0
150	-351.589	2.1
180	-351.516	9.2

Table S3. Predicted (ADF) NMR chemical shifts in ppm for the four carbonyl nuclei of the dimer as a function of the (bipyridine-bipyridine) staggering angle. Theoretical NMR chemical shifts $\{\delta_{ADF}\}$ were computed from $\delta_{ADF} = -0.7618 \times \sigma_{ADF} + 173.59$ (obtained from both monomer and dimer data).

Dimer	C11		C12		C23		C24	
Angle	σ_{ADF}	δ_{ADF}	σ_{ADF}	δ_{ADF}	σ_{ADF}	δ_{ADF}	σ_{ADF}	δ_{ADF}
0°	-40.59	204.4	-41.16	204.9	-40.69	204.6	-41.07	204.9
30°	-43.59	206.7	-41.61	205.3	-40.86	204.7	-44.59	207.6
60°	-42.86	206.2	-42.25	205.8	-42.30	205.8	-42.91	206.3
90°	-40.55	204.4	-40.75	204.6	-40.25	204.3	-41.13	204.9
120°	-41.98	205.5	-42.48	206.0	-42.46	205.9	-42.24	205.8
150°	-40.64	204.5	-43.89	207.0	-43.51	206.7	-40.43	204.4
180°	-41.48	205.1	-41.60	205.3	-41.50	205.2	-41.60	205.3

Table S4. Formal charges (2/n) and computed Hirshfeld (Q_{Hirs}) charges for the whole series n=1-5 (from monomer to pentamer).

n=	1		2		3		4		5	
C=O	(2/n)	Q_{Hirs}	(2/n)	Q_{Hirs}	(2/n)	Q_{Hirs}	(2/n)	Q_{Hirs}	(2/n)	Q_{Hirs}
C11/12	2	0.2415	1	0.1736	0.667	0.1842	0.5	0.1841	0.4	0.1848
C23/24	n/a		1	0.1742	0.667	0.1156	0.5	0.1246	0.4	0.1287
C35/36			n/a		0.667	0.1850	0.5	0.1255	0.4	0.1375
C47/48					n/a		0.5	0.1845	0.4	0.1282
C59/60							n/a		0.4	0.1843
average	0.2415		0.1739		0.1616		0.1547		0.1527	

Table S5. Computed (non relativist) screening constants $\{\sigma_{ADF}\}$ and predicted chemical shifts $\{\delta_{ADF}\}$ in ppm for carbonyls for the whole series n=1-5 (from monomer to pentamer). To estimate the chemical shifts, we relied on the following (non relativistic) correlation: $\delta_{ADF} = -0.7618 \times \sigma_{ADF} + 173.59$ ($R^2 = 0.9884$) (obtained from both monomer and dimer data).

n=	1		2		3		4		5	
C=O	σ_{ADF}	δ_{ADF}	σ_{ADF}	δ_{ADF}	σ_{ADF}	δ_{ADF}	σ_{ADF}	δ_{ADF}	σ_{ADF}	δ_{ADF}
C11	-34.78	200.1	-40.84	204.7	-42.97	206.3	-40.60	204.5	-40.39	204.4
C12	-34.71	200.0	-43.60	206.8	-42.97	206.3	-43.24	206.5	-43.17	206.5
C23	n/a		-43.37	206.6	-45.56	208.3	-45.24	208.1	-44.96	207.9
C24			-40.86	204.7	-46.07	208.7	-45.67	208.4	-44.83	207.8
C35			n/a		-43.13	206.4	-45.97	208.6	-44.10	207.2
C36					-40.74	204.6	-45.76	208.5	-44.13	207.2
C47					n/a		-43.34	206.6	-44.87	207.8
C48							-40.62	204.5	-45.21	208.0
C59							n/a		-43.25	206.5
C60									-40.29	204.3

REFERENCES.

(1) E. Pretsch, T. Clerc, J. Seible, W. Simon, "Tabellen zur Strukturaufklärung organischer Verbindungen mit specktroskopischen Methoden", 3rd edition, Berlin; Heidelberg; New York; Tokyo : Springer, 1986. (Anleitung für die chemische Laboratoriumspraxis; vol. 15) ISBN 3-540-15895-2 (Berlin) ISBN 0-387-15895-2 (New York)