Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for: Direct observation of the solvent organization and nuclear vibrations of $[Ru(dcbpy)_2(NCS)_2]^{4-}$, [dcbpy = (4,4'-dicarboxy-2,2'-bipyridine)], via *ab initio* molecular dynamics

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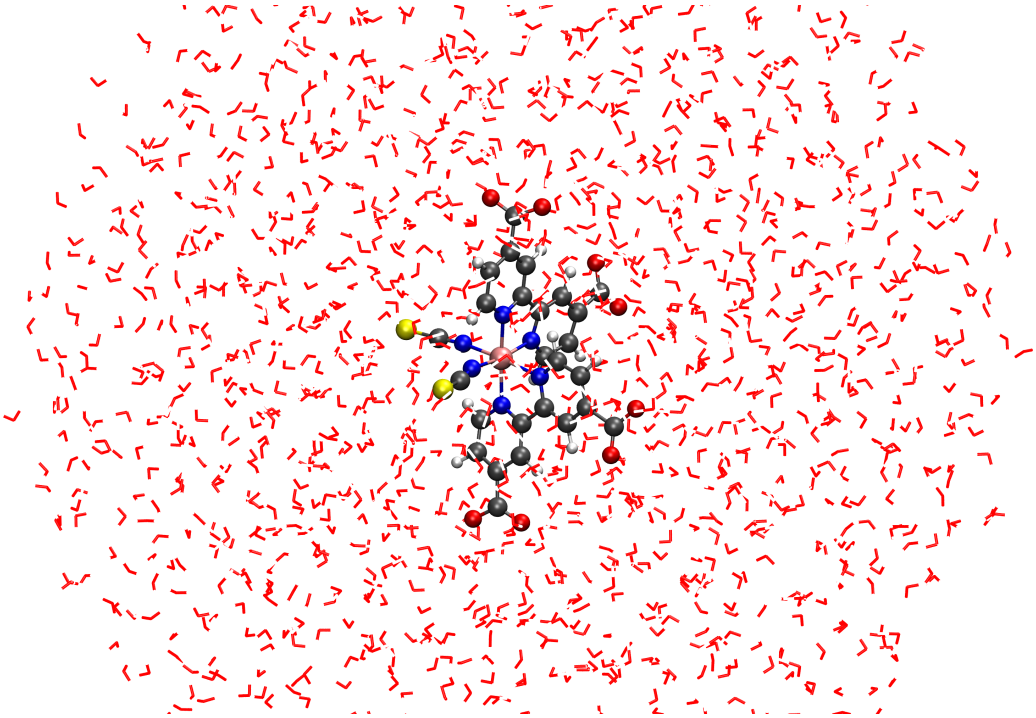

Figure S1: $N3^{4-}$ in a spherical water box. The solute (represented as ball-and-stick) is treated at a QM level, while the surrounding solvent (represented as lines) at a MM level.

Table S1: Mulliken population analysis on 10wat/CPCM cluster at the B3LYP/SDD/def2-SVP level of theory. The total charges of the $N3^{4-}$ solute and the ten surrounding water molecules are also shown. The atomic charges are in atomic units. Atom labels are defined in Fig. S2.

	$N3^{4-}$			**10 water**	
atom	charge	atom	charge	atom	charge
C1	0.1630	H29	-0.0963	H56	0.1466
C2	0.1142	C30	-0.0258	O57	-0.3171
C3	-0.0467	H31	0.0426	H58	0.1677
C4	0.1442	H32	-0.0710	H59	0.1465
C5	-0.0247	N33	-0.2019	O60	-0.3168
H6	0.0425	N34	-0.2021	H61	0.1676
C7	0.0210	N35	-0.2051	H62	0.1648
H8	-0.0963	N36	-0.2051	O63	-0.3453
C9	-0.0649	N37	0.0103	H64	0.1598
H10	-0.0719	C38	-0.1859	H65	0.1725
C11	0.1240	S39	-0.4087	O66	-0.3389
C12	0.0228	Ru40	0.3097	H67	0.1730
H13	-0.0344	N41	0.0106	H68	0.1615
C14	-0.0282	C42	-0.1860	O69	-0.3666
H15	-0.0067	S43	-0.4088	H70	0.1263
H16	-0.0720	C44	0.1604	H71	0.1661
C17	0.1441	C45	0.1780	O72	-0.3436
C18	0.1237	C46	0.1607	H73	0.1592
C19	-0.0643	C47	0.1780	H74	0.1647
C20	0.1636	O48	-0.4036	O75	-0.3455
C21	-0.0282	O49	-0.3867	H76	0.1602
H22	-0.0067	O50	-0.3961	H77	0.1721
C23	0.0232	O51	-0.3877	O78	-0.3388
H24	-0.0349	O52	-0.4035	H79	0.1732
C25	-0.0471	O53	-0.3867	H80	0.1618
H26	-0.0721	O54	-0.3875	O81	-0.3667
C27	0.1141	O55	-0.3965	H82	0.1262
C28	0.0217			H83	0.1663
				O84	-0.3440
				H85	0.1595
total			-3.7728		-0.2272
			(94.32%)		(5.68%)

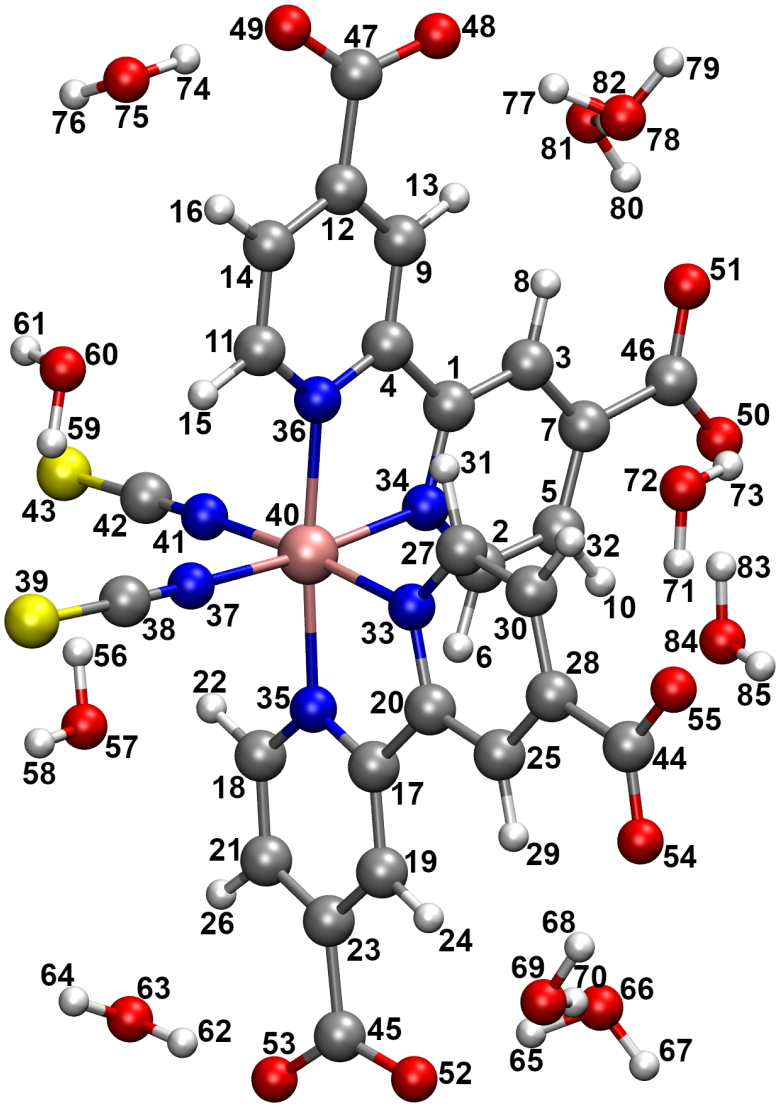

Figure S2: Optimized $N3^{4-}$ 10wat/CPCM cluster. In this model, each $N3^{4-}$ solvation site interacts with one water molecule. Atom labels are also shown.

Table S2: S(NCS)-O(wat) and O(dcbpy)-O(wat) radial distributions maxima $r_{\max}$ and integrated number of solvent molecules in the first shell. Labels are defined in Fig. S3.

	$r_{\max}$ (Å)	n_{wat}
S39	3.10	4.49
S43	3.10	4.38
O48	2.70	2.83
O49	2.70	3.51
O50	2.70	3.03
O51	2.70	3.70
O52	2.70	3.48
O53	2.70	3.16
O54	2.70	3.66
O55	2.70	3.10

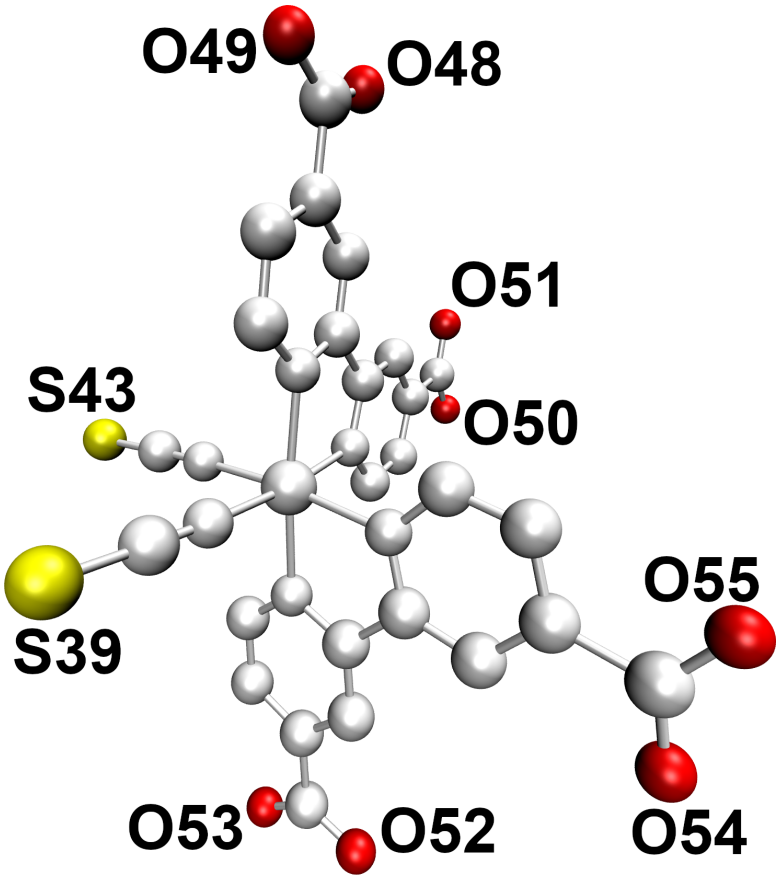

Figure S3: $N3^{4-}$ solvation sites. Dcbpy oxygen and NCS^{-} sulfur atoms are highlighted in red and yellow, respectively.

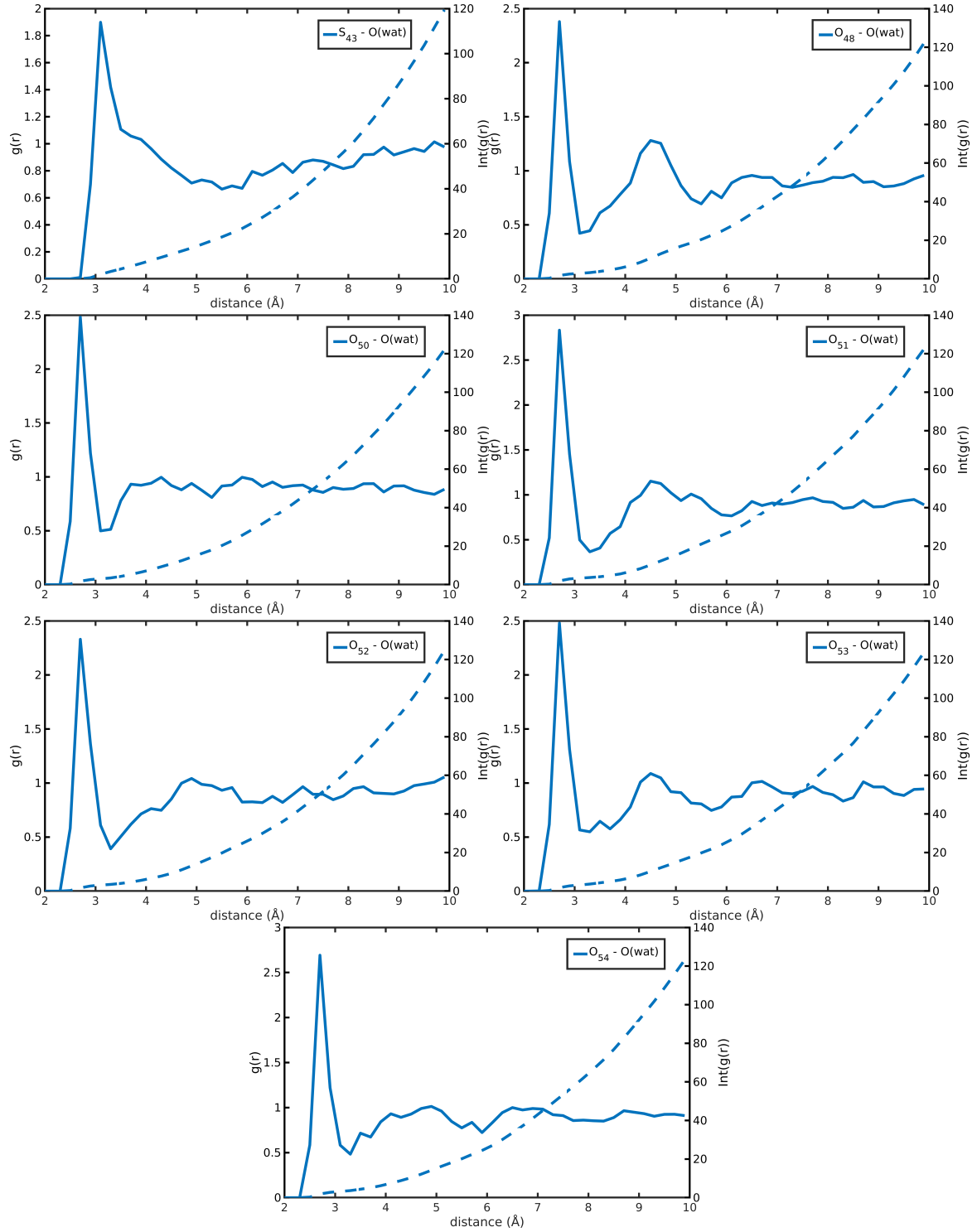

Figure S4: S(NCS)-O(wat) and O(dcbpy)-O(wat) radial distribution functions for several $N3^{4-}$ solvation sites.

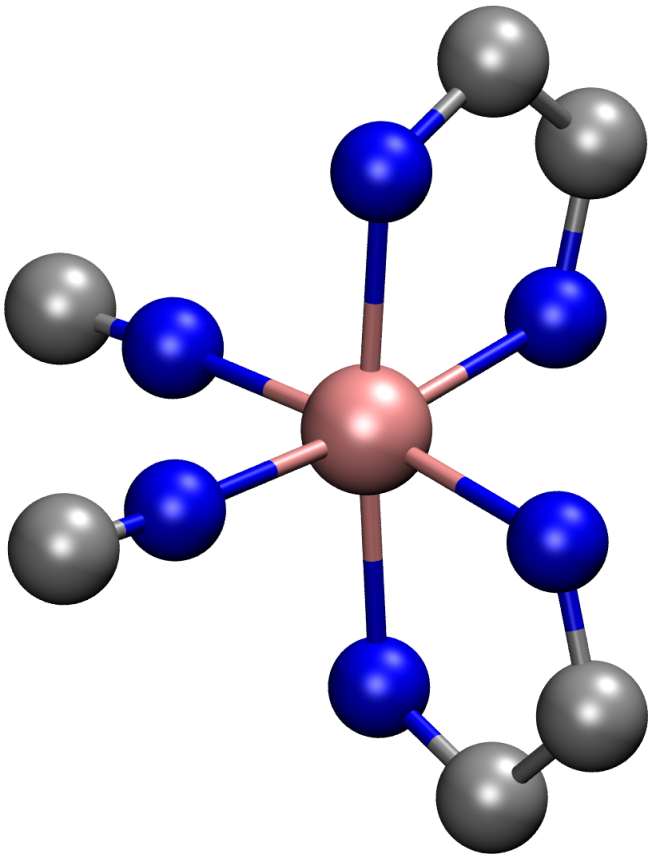

Figure S5: A reduced $N3^{4-}$ model for C_2 continuous symmetry measure (CSM) calculations. For NCS^- ligands, N and C atoms are retained; for dcbpy ligands, N-C-C-N bonded atoms are retained. Keeping dcbpy chelation (although in a simplified form) allows this reduced model to assume a symmetry not higher than C_2, as the full $N3^{4-}$ structure.