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

Supporting Information

	Simplified Complexes	Substituted Complexes	Difference
	$\bar{r}_{U-N}$	$\bar{r}_{U-N}$	$\Delta\bar{r}_{U-N}$
C_0	2.532/*2.527*	2.554/*2.543*	0.022/*0.016*
C_2a	2.804/*2.799*	2.673/*2.659*	0.131/*0.140*
C_2b	2.780/*2.771*	2.688/*2.674*	0.112/*0.097*
C_2c	2.776/*2.770*	2.689/*2.674*	0.087/*0.096*
C_4a	2.717/*2.706*	2.689/*2.680*	0.028/*0.026*
C_4b	2.701/*2.687*	2.684/*2.673*	0.017/*0.014*
C_4c	2.703/*2.692*	2.689/*2.678*	0.014/*0.014*
C_6	2.700/*2.697*	2.696/*2.688*	0.004/*0.009*

Table S1: Average U-N bond lengths in Angstrom for complexes optimised with the PBE exchange correlation functional in the gas phase/*DCM*, with and without peripheral substituents.

	$r_{U\text{-}N}$ (Gas phase/*DCM*)						$r_{U\text{-}N}$ (Exp)			
	$r_{U\text{-}N}$	$r_{U\text{-}N}$	$r_{U\text{-}N}$	$r_{U\text{-}N}$	$r_{U\text{-}N}$	$r_{U\text{-}N}$	$r_{U\text{-}N1}$	$r_{U\text{-}N2}$	$r_{U\text{-}N3}$	$r_{U\text{-}N(av)}$
C_0	2.534/*2.530*	2.528/*2.522*	-	-	-	-	-	-	-	2.53[a]
C_2a'	2.835/*2.812*	2.709/*2.696*	2.709/*2.694*	2.604/*2.591*	2.593/*2.581*	2.591/*2.579*	-	-	-	-
C_2b'	2.586/*2.573*	2.587/*2.573*	2.772/*2.702*	2.765/*2.693*	2.713/*2.755*	2.705/*2.747*	2.57	2.68	2.64	2.63[b]
C_2c'	2.751/*2.736*	2.749/*2.733*	2.749/*2.733*	2.749/*2.732*	2.569/*2.557*	2.569/*2.557*	-	-	-	-
C_4a	2.827/*2.811*	2.763/*2.754*	2.593/*2.578*	2.533/*2.527*	-	-	-	-	-	-
C_4b	2.720/*2.700*	2.692/*2.682*	2.690/*2.678*	-	-		-	-	-	-
C_4c	2.785/*2.769*	2.663/*2.654*	-	-	-	-	-	-	-	-
C_6	2.820/*2.818*	2.640/*2.637*	-	-	-	-	-	-	-	-

Table S2: Distinct U-N bond lengths in Angstrom for complexes optimised using the PBE exchange-correlation functional in the gas phase/*DCM*. Experimental data obtained from refs: a) [44], b) [45].

	r_{U-N1}	r_{U-N2}	r_{U-N3}	r_{U-N4}	r_{U-N5}	r_{U-N6}	$\overline{r_{U-N}}$
C_0	2.538/ *2.534*	2.538/ *2.534*	2.530/ *2.523*	2.538/ *2.534*	2.538/ *2.534*	2.530/ *2.523*	2.535/ *2.530*
C_2b'	2.602/ *2.586*	2.601/ *2.586*	2.790/ *2.773*	2.785/ *2.766*	2.726/ *2.716*	2.724/ *2.710*	2.704/ *2.689*
C_4a	2.615/ *2.599*	2.859/ *2.842*	2.788/ *2.777*	2.546/ *2.539*	2.788/ *2.777*	2.859/ *2.842*	2.742/ *2.723*
C_6	2.854/ *2.817*	2.661/ *2.637*	2.661/ *2.637*	2.854/ *2.817*	2.661/ *2.637*	2.661/ *2.637*	2.725/ *2.697*

Table S3: U-N bond lengths in Angstrom for complexes optimised using the B3LYP exchange-correlation functional in the gas phase/*DCM*.

	r_{U-O1}	r_{U-O2}
C_0	1.781/*1.794*	1.871/*1.794*
C_2b'	1.766/*1.777*	1.766/*1.777*
C_4a	1.762/*1.770*	1.762/*1.770*
C_6	1.764/*1.796*	1.761/*1.790*

Table S4: U-O bond lengths in Angstrom for complexes optimised using the B3LYP exchange-correlation functional in the gas phase/*DCM*.

	ΔE	ΔE_{DA}	E_{DL}	E^{DU}
C_0	-29.13	-30.23	0.69	0.40
C_2b'	-27.78	-29.02	0.96	0.28
C_4a	-26.00	-28.18	1.93	0.25
C_6	-25.76	-27.84	1.83	0.25

Table S5: Molecular binding energies and deformation adjusted binding energies, with deformation energies of the UO_2^{2+} unit and the ligands, all given in eV. Data was obtained using the B3LYP *xc*-functional, and due to the simple COSMO solvation model being a rather poor approximation for solvated uncoordinated UO_2^{2+}, are given in the gas phase only.

	C_0	C_2b'	C_4a	C_6
$\sum \rho_{U-N}$	0.356	0.264	0.251	0.251
$\nabla^2 \bar{\rho}_{U-N}$	0.148	0.108	0.102	0.103
$\sum H_{U-N}$	-0.044	-0.022	-0.021	-0.019
$\sum \delta(U,N)$	2.226	1.922	1.838	1.820

Table S6: various topological parameters measured at the bond critical points of the U-N bonds, measured in atomic units (a.u) given as total or average values, and total indices of delocalisation between the U-N atomic basins given as a proportion of a pair of electrons. Data is from structures calculated using the PBE functional including the effects of solvation in DCM using COSMO.

	C_0	C_2b'	C_4a	C_6	
				U-O_1	U-O_2
ρ_{U-O}	0.281	0.290	0.294	0.295	0.292
$\nabla^2 \rho_{U-O}$	0.323	0.254	0.316	0.325	0.310
H_{U-O}	-0.238	-0.316	-0.261	-0.263	-0.259
$\delta(U,O)$	1.872	1.928	1.946	1.934	1.935

Table S7: Various topological parameters measured at the bond critical points of the U-O bond measured in atomic units (a.u). Data is from structures calculated using the PBE *xc*-functional including the effects of solvation in DCM using COSMO.

	C_0	C_2b'	C_4a	C_6
$\sum \rho_{U-N}$	0.344/*0.352*	0.244/*0.255*	0.230/*0.238*	0.234/*0.248*
$\nabla^2 \bar{\rho}_{U-N}$	0.152/*0.151*	0.105/*0.107*	0.098/*0.100*	0.101/*0.106*
$\sum H_{U-N}$	-0.040/*-0.043*	-0.017/*-0.020*	-0.016/*-0.018*	-0.016/*-0.019*
$\sum \delta(U,N)$	1.970/*2.053*	1.629/*1.740*	1.558/*1.627*	1.561/*1.665*

Table S8: various topological parameters measured at the bond critical points of the U-N bonds, measured in atomic units (a.u) given as total or average values, and total indices of delocalisation between the U-N atomic basins given as a proportion of a pair of electrons. Data is from structures calculated using the B3LYP functional in the gas phase/DCM.

	C_0	C_2b'	C_4a	C_6	
				U-O_1	U-O_2
ρ_{U-O}	0.304/*0.295*	0.317/*0.308*	0.320/*0.313*	0.320/*0.299*	0.319/*0.295*
$\nabla^2\rho_{U-O}$	0.274/*0.278*	0.265/*0.267*	0.264/*0.266*	0.273/*0.281*	0.257/*0.265*
H_{U-O}	-0.281/-*0.265*	-0.303/-*0.287*	-0.309/-*0.297*	-0.309/-*0.271*	-0.307/-*0.265*
$\delta(U,O)$	1.872/*1.831*	1.936/*1.897*	1.945/*1.915*	1.936/*1.890*	1.926/*1.887*

Table S9: Various topological parameters measured at the bond critical points of the U-O bond measured in atomic units (a.u). Data is from structures calculated using the B3LYP xc-functional in the gas phase/DCM.

C_6	PBE, DCM	B3LYP, gas phase	B3LYP, DCM
ρ_{O-Cm}	0.009	0.008	0.009
$\nabla^2\rho_{O-Cm}$	0.038	0.035	0.038
H_{O-Cm}	0.002	0.002	0.002
$\delta(O_1,Cm)$	0.034	0.029	0.033
$\delta(O_2,N)$	0.092	0.087	0.092

Table S10: Various topological parameters measured at the bond critical points of the O-C_m interactions of C_6, given as average values. Measured in atomic units (a.u). Data is from structures calculated using the PBE *xc*-functional including the effects of solvation in DCM with COSMO and the B3LYP *xc*-functional both in the gas phase and including the effects of solvation in DCM with COSMO.

	UO_2^{2+}	C_0	C_2b'	C_4a	C_6
N(U)	88.70	89.19	89.18	89.17	89.18
N(O_1)	8.65	8.90	8.89	8.87	8.87,8.86
λ(U)	86.45	86.04	86.11	86.13	86.14
λ(O)	7.47	7.77	7.75,7.74	7.70	7.67,7.64
δ(U,O)	2.24	1.87	1.93	1.94	1.94,1.93
δ(O_1,O_2)	0.13	0.10	0.10	0.10	0.10
N(UO_2)	106.00	106.99	106.95	106.91	106.90
λ(UO_2)	106.00	105.43	105.56	105.53	105.42
N(UO_2)- λ(UO_2)	0.00	1.56	1.39	1.39	1.49

Table S11: Integrated properties associated with the uranyl ions of each complex given to 2 decimal places. Data from complexes optimised using the PBE *xc*-functional including the effects of solvation in DCM with COSMO.

	UO_2^{2+}	C_0	C_2b'	C_4a	C_6
N(U)	88.71	88.98	88.96	88.95	88.96
N(O)	8.65	8.91	8.89	8.88	8.88
λ(U)	86.44	86.01	86.09	86.11	86.12
$\lambda(O_2)$	7.45	7.80	7.76	7.73	7.71,7.69
δ(U,O)	2.27	1.87	1.94	1.95	1.94,1.93
$\delta(O_1,O_2)$	0.11	0.09	0.10	0.10	0.09
$N(UO_2)$	106.00	106.81	106.74	106.72	106.72
$\lambda(UO_2)$	106.00	105.44	105.59	105.57	105.47
$N(UO_2)$- $\lambda(UO_2)$	0.00	1.37	1.15	1.15	1.26

Table S12: Integrated properties associated with the uranyl ions of each complex given to 2 decimal places. Data from complexes optimised using the B3LYP *xc*-functional in the gas phase.

	UO_2^{2+}	C_0	C_2b'	C_4a	C_6
N(U)	88.56	88.98	88.96	88.95	88.98
N(O)	8.72	8.95	8.92	8.91	8.91,8.90
λ(U)	86.37	86.00	86.08	86.10	86.11
λ(O)	7.57	7.86	7.81	7.77	7.74,7.71
$\delta(U,O_1)$	2.19	1.83	1.90	1.91	1.89
$\delta(O_1,O_2)$	0.11	0.09	0.09	0.09	0.09
$N(UO_2)$	106.00	106.88	106.81	106.77	106.79
$\lambda(UO_2)$	106.00	105.46	105.59	105.56	105.43
$N(UO_2)$- $\lambda(UO_2)$	0.00	1.42	1.22	1.21	1.36

Table S13: Integrated properties associated with the uranyl ions of each complex given to 2 decimal places. Data from complexes optimised using the B3LYP *xc*-functional including the effects of solvation in DCM with COSMO.

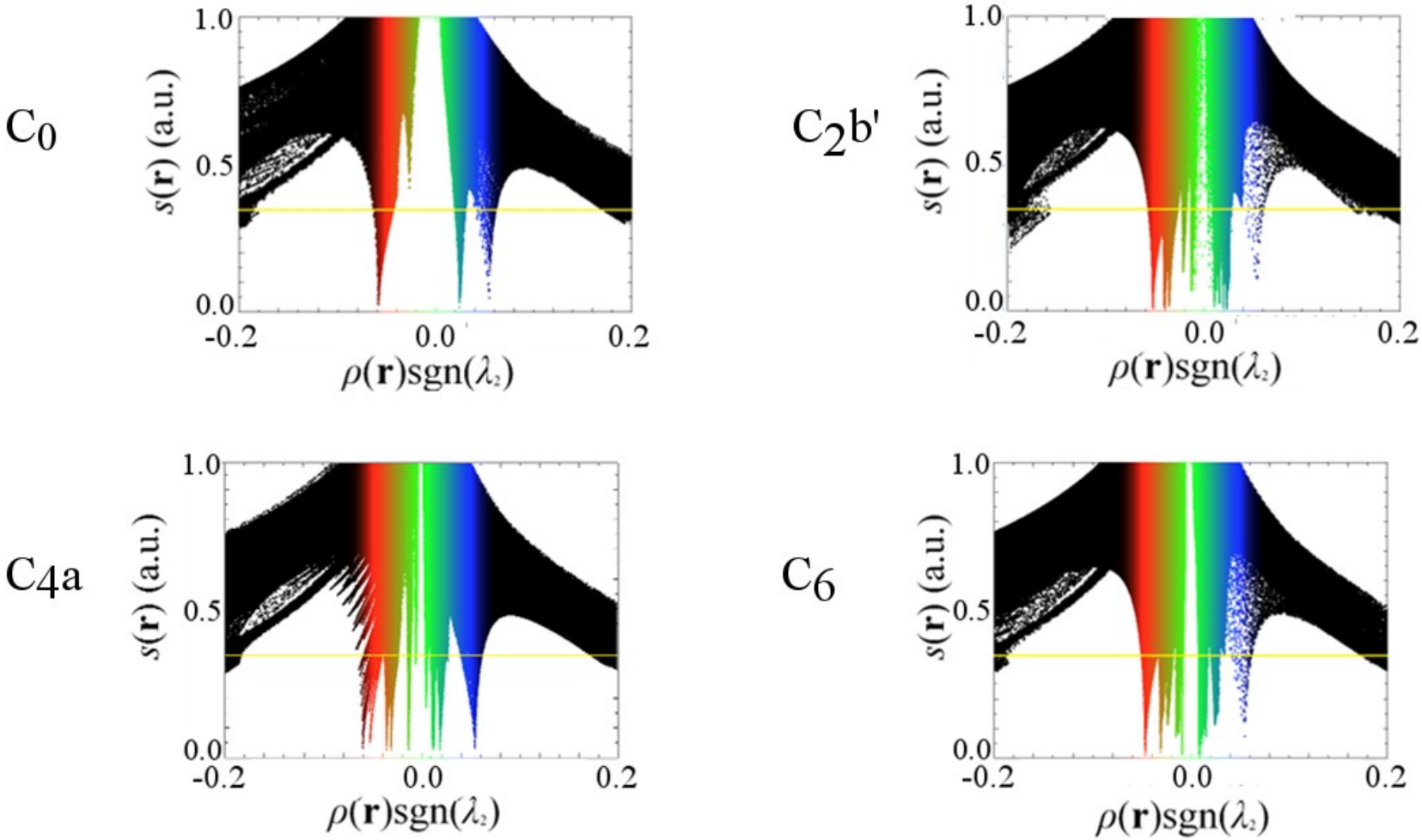

Figure S1: Scatter plots of the reduced density gradient against $\rho(\mathbf{r})\mathrm{sgn}(\lambda_2)$ coloured with values of $\rho(\mathbf{r})\mathrm{sgn}(\lambda_2)$ from the isosurfaces in Figure 9. Horizontal lines indicate isosurface value of $s(\mathbf{r})$ = 0.35 a.u. from Figure 9.

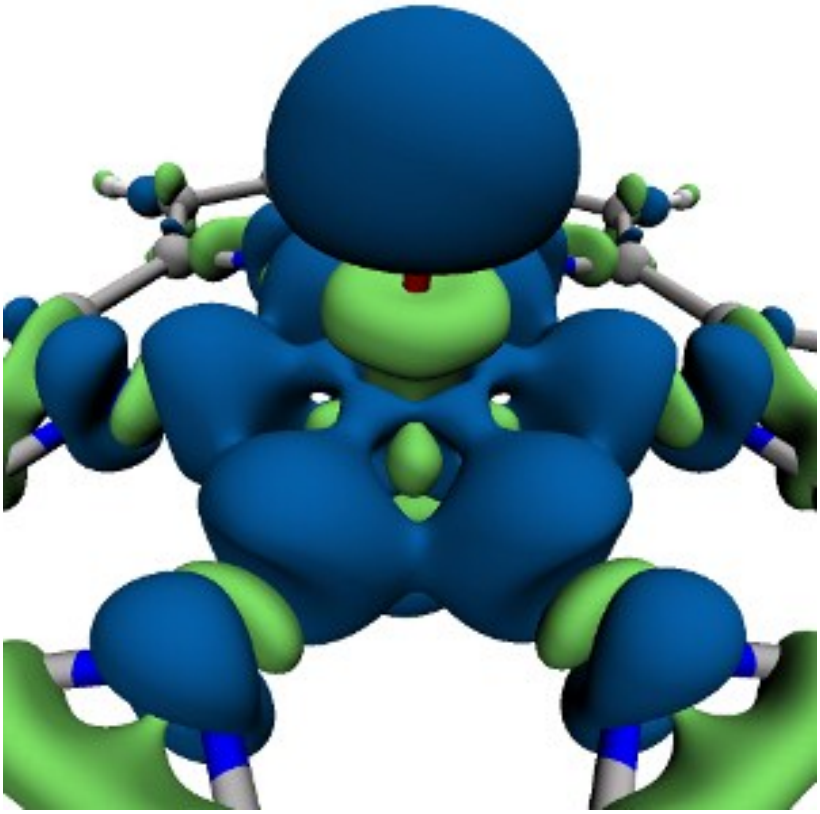

Figure S2: Close up view of the U-N bonding region in a density difference distribution from C_0, showing teardrop-shaped regions of accumulation (blue) and depletion (green) around the uranium atom.