Electronic Supplementary Material (ESI) for Dalton Transactions

Supplementary Information

Theoretical exploration of uranyl complexes of a designed polypyrrolic macrocycle: Structure/property effects of hinge size on Pacman-shaped complexes †

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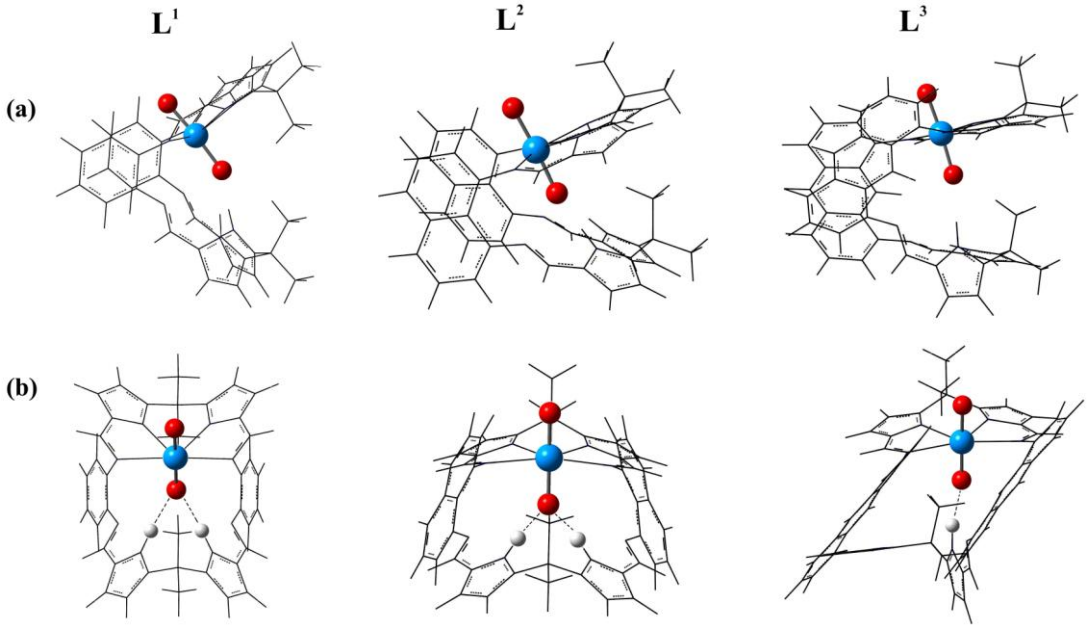

Fig. S1 Structures of the mononuclear $[(UO_2)(H_2L^x)]^{n-2}$ ($L^x = L^1$, L^2 and L^3; n = 2 for U^{VI}; n = 1 for U^V) complexes, (a) side-on view, (b) face-on view.

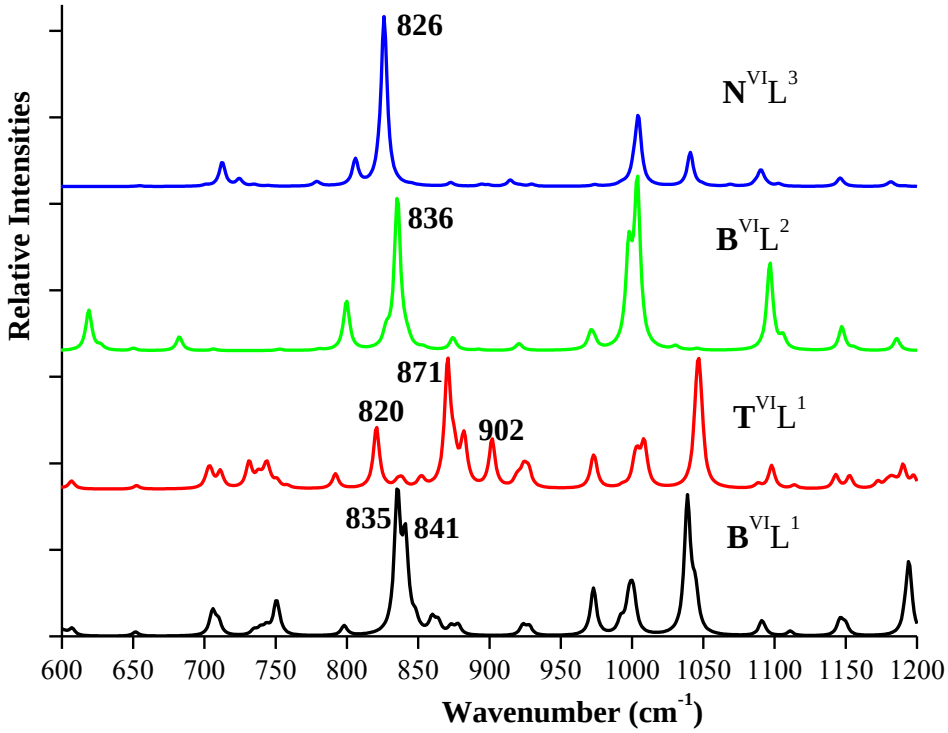

Fig. S2. Simulated vibrational spectra of binuclear $[(U^{VI}O_2)_2(L^x)]$ ($L^x = L^1$, L^2 and L^3) complexes. For convenient comparison, the calculated intensities of $\mathbf{T}^{VI}L^1$ and $\mathbf{B}^{VI}L^1$ are scaled by a factor of 0.05, and those of $\mathbf{B}^{VI}L^1$ are scaled by 2.

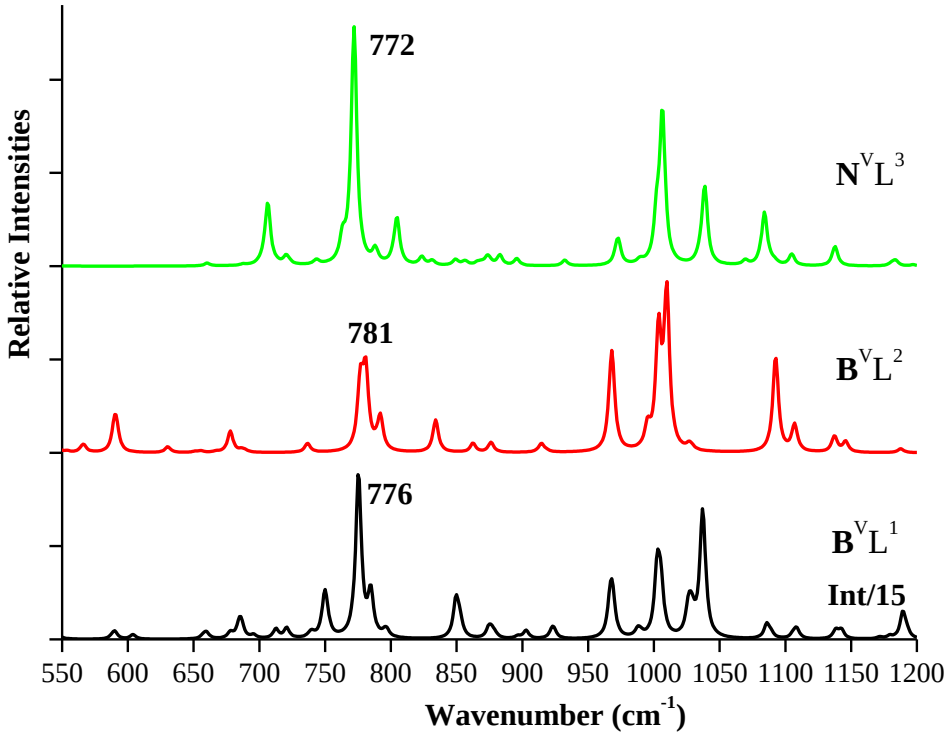

Fig. S3. Simulated vibrational spectra of binuclear $[(U^{V}O_2)_2(L^{x})]^{2-}$ (L^{x} = L^{1}, L^{2} and L^{3}) complexes. For convenient comparison, the calculated intensities of $\mathbf{B}^{V}L^{1}$ are scaled by a factor of 1/15.

Table S1 Optimized geometry parameters and bond orders (in parentheses) for mononuclear complexes, $[(UO_2)(S)(H_2L^2)]^{n-2}$ (Solvent = Vacant and py; n = 2 for U^{VI}, n = 1 for U^{V}) in the gas phase.

Complexes	S =	U-O_{exo}	U-O_{endo}	U-N_{eq}	$O_{endo}\cdots H$	O=U=O
S**M**$^{VI}L^2$	Vacant	1.806 (2.38)	1.830 (2.19)		1.942 (0.07)	176.6
	py	1.808 (2.39)	1.836 (2.15)	2.612 (0.37)	1.881 (0.08)	175.5
S**M**$^{V}L^2$	Vacant	1.835 (2.38)	1.882 (2.04)		1.814 (0.12)	176.9
	py	1.839 (2.38)	1.887 (2.02)	2.553 (0.45)	1.782 (0.12)	176.8

Table S2 Optimized geometry parameters and bond orders (in parentheses) for mononuclear $[(UO_2)(H_2L^x)]^{n-2}$ ($L^x = L^1$, L^2 and L^3; n = 2 for U^{VI}; n = 1 for U^{V}) in the gas phase. (Bond lengths in Å and angles in degree)

Complexes		U-O_{exo}	U-O_{endo}	$O_{endo}\cdots H$	O-U-O
M$^{VI}L^1$	Cal.	1.796 (2.43)	1.832 (2.19)	2.051 (0.05)	175.4
	Expt. [a.]	1.766	1.790	2.251	177.6
M$^{V}L^1$	Cal.	1.823 (2.43)	1.889 (2.01)	1.856 (0.11)	174.7
M$^{VI}L^2$	Cal.	1.806 (2.38)	1.830 (2.19)	1.942 (0.07)	176.6
M$^{V}L^2$	Cal.	1.835 (2.38)	1.882 (2.04)	1.814 (0.12)	176.9
M$^{VI}L^3$	Cal.	1.801 (2.40)	1.817 (2.30)	2.034 (0.05)	176.3
M$^{V}L^3$	Cal.	1.830 (2.39)	1.853 (2.24)	1.946 (0.08)	173.6

[a.] Experimental values for $[(UO_2)(THF)(H_2L^1)]$ from ref. [9].

Table S3 Calculated electron-spin densities and atomic charges (in parentheses) for mononuclear $[(UO_2)(H_2L^x)]^{n-2}$ ($L^x = L^1$, L^2 and L^3; n = 2 for U^{VI}; n = 1 for U^V) complexes in the gas phase.

Complexes	U	O_{exo}	O_{endo}	H
$\mathbf{M}^{VI}L^1$	0.000 (1.339)	0.000 (-0.254)	0.000 (-0.380)	0.000 (0.201)
$\mathbf{M}^{V}L^1$	0.993 (1.150)	-0.043 (-0.312)	-0.035 (-0.470)	0.000 (0.214)
$\mathbf{M}^{VI}L^2$	0.000 (1.389)	0.000 (-0.283)	0.000 (-0.371)	0.000 (0.207)
$\mathbf{M}^{V}L^2$	0.964 (1.210)	-0.040 (-0.339)	-0.035 (-0.453)	0.001 (0.221)
$\mathbf{M}^{VI}L^3$	0.000 (1.397)	0.000 (-0.270)	0.000 (-0.328)	0.000 (0.222)
$\mathbf{M}^{V}L^3$	0.756 (1.224)	-0.033 (-0.321)	-0.031 (-0.388)	0.000 (0.230)

Table S4 Optimized geometry parameters and bond orders (in parentheses) for binuclear $[(UO_2)_2(L^x)]^{2n-4}$ ($L^x = L^1$ and L^2; n = 2 for U^{VI}; n = 1 for U^V) in the gas phase. (Bond lengths in Å and angles in degree)

Compl.	U_1-O_{exo}	U_1-O_{endo}	U_2-O_{exo}	U_2-O_{endo}	$U_1\cdots U_2$	O_{exo}-U_1-O_{endo}	O_{exo}-U_2-O_{endo}	U_1-O_{endo}-U_2
$\mathbf{B}^{VI}L^1$	1.818	2.111/2.093	1.814	2.144/2.070	3.377	176.6/104.1	175.6/102.7	
	(2.44)	(1.21/1.18)	(2.45)	(1.19/1.18)	(0.33)			
$\mathbf{T}^{VI}L^1$	1.805/1.801	2.387	1.806	1.847	4.214	179.3/101.5	169.9	168.9
	(2.40/2.38)	(0.37)	(2.40)	(2.00)	(0.09)			
$\mathbf{B}^{V}L^1$	1.858	2.107/2.144	1.853	2.151/2.078	3.399	176.3/103.1	175.7/102.0	
	(2.42)	(1.25/1.09)	(2.43)	(1.12/1.25)	(0.49)			
$\mathbf{B}^{VI}L^2$	1.822	2.099/2.082	1.819	2.133/2.048	3.363	176.7/110.4	178.9/108.2	
	(2.44)	(1.26/1.11)	(2.43)	(1.15/1.21)	(0.32)			
$\mathbf{B}^{V}L^2$	1.853	2.124/2.084	1.854	2.138/2.093	3.370	177.5/108.3	178.5/107.8	
	(2.42)	(1.21/1.17)	(2.41)	(1.16/1.17)	(0.43)			

Table S5 Optimized geometry parameters and bond orders (in parentheses) for binuclear $[(UO_2)_2(L^3)]^{2n-4}$ (n = 2 for U^{VI}; n = 1 for U^{V}) in the gas phase. (Bond lengths in Å and angles in degree)

Complexes	U-O_{exo}	U-O_{endo}	U···O_{endo}	O_{endo}···O_{endo}	O_{exo}-U-O_{endo}
$\mathbf{N}^{VI}L^3$	1.802 (2.39)	1.798 (2.38)	3.931	2.940	175.6
$\mathbf{N}^{V}L^3$	1.827 (2.38)	1.817 (2.37)	4.043	3.116	176.1

Table S6 Calculated electron-spin densities and atomic charges for binuclear $[(UO_2)_2(L^x)]^{2n-4}$ (L^x = L^1, L^2 and L^3; n = 2 for U^{VI}; n = 1 for U^{V}) complexes in the gas phase.

	U1		U2	
	electron-spin densities	atomic charges	electron-spin densities	atomic charges
$\mathbf{B}^{VI}L^1$	0.000	1.406	0.000	1.376
$\mathbf{T}^{VI}L^1$	0.000	1.272	0.000	1.459
$\mathbf{B}^{V}L^1$	1.093	1.136	0.978	1.121
$\mathbf{B}^{VI}L^2$	0.000	1.444	0.000	1.474
$\mathbf{B}^{V}L^2$	0.975	1.204	1.042	1.217
$\mathbf{N}^{VI}L^3$	0.000	1.414	0.000	1.414
$\mathbf{N}^{V}L^3$	0.563	1.263	0.564	1.263