Supporting Information for:

Synthesis, Characterization, and Density Functional Theory Analysis of Uranium and Thorium Complexes Containing Nitrogen-rich 5-methyltetrazolate Ligands

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Table S1. Comparison of bond lengths and angles for the calculated and crystal structures of $(C_5Me_5)_2U[\eta^2\text{-}(N,N')\text{-tetrazolate}]_2$ (**7**) and $(C_5Me_5)_2Th[\eta^2\text{-}(N,N')\text{-tetrazolate}]_2$ (**8**). Bond lengths in Å and angles in degrees.

	$(C_5Me_5)_2U[\eta^2\text{-}(N,N')\text{-tetrazolate}]_2$ (7)		$(C_5Me_5)_2Th[\eta^2\text{-}(N,N')\text{-tetrazolate}]_2$ (**8**)	
	Exp.	Calc.	Exp.	Calc.
An–N(1)	2.456(2)	2.471	2.5244(19)	2.475
An–N(2)	2.457(2)	2.485	2.5008(18)	2.610
An–N(5)	2.427(2)	2.485	2.4912(18)	2.506
An–N(6)	2.492(3)	2.466	2.5402(18)	2.519
N(1)–N(2)	1.349(3)	1.344	1.357(3)	1.348
N(2)–N(3)	1.315(3)	1.302	1.315(3)	1.309
N(3)–N(4)	1.341(4)	1.338	1.340(3)	1.326
N(4)–C(21)	1.334(4)	1.337	1.344(3)	1.345
N(1)–C(21)	1.339(3)	1.339	1.334(3)	1.335
N(5)–N(6)	1.352(3)	1.345	1.351(3)	1.346
N(6)–N(7)	1.303(4)	1.302	1.310(3)	1.303
N(7)–N(8)	1.353(4)	1.338	1.353(3)	1.335
N(8)–C(23)	1.339(4)	1.337	1.331(3)	1.339
N(5)–C(23)	1.336(3)	1.339	1.335(3)	1.338
C(1)–C(2)	1.422(4)	1.422	1.424(3)	1.424
C(2)–C(3)	1.424(4)	1.423	1.423(3)	1.424
C(3)–C(4)	1.420(4)	1.424	1.421(3)	1.424
C(4)–C(5)	1.415(4)	1.424	1.413(3)	1.424
C(1)–C(5)	1.422(4)	1.423	1.426(3)	1.422
C(11)–C(12)	1.420(4)	1.424	1.433(3)	1.424
C(12)–C(13)	1.426(3)	1.423	1.415(3)	1.424
C(13)–C(14)	1.421(4)	1.424	1.421(3)	1.424
C(14)–C(15)	1.419(4)	1.422	1.422(3)	1.422
C(11)–C(15)	1.429(4)	1.422	1.422(3)	1.424
An(1)–C_{cent}	2.447(3)	2.506	2.511(2)	2.577
An(1)–C_{cent}'	2.444(3)	2.505	2.514(2)	2.577
N(1)–An(1)–N(2)	31.86(7)	31.51	31.33(6)	30.60
N(5)–An(1)–N(6)	31.87(8)	31.47	31.13(6)	31.08
N(1)/N(2)–An(1)–N(5)	80.01(8)	80.51	77.73(6)	79.37
C_{cent}–An(1)–$C_{cent'}$	140.2(1)	150.9	136.65(7)	137.9

Complete author list for reference 25 (Gaussian 09) in Main Text

Gaussian 09, Revision **D.01**, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, 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, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

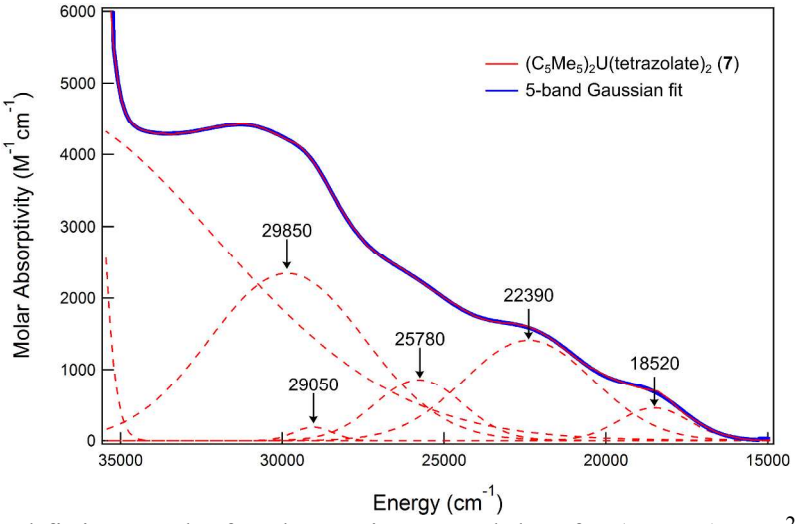


Figure S1. Spectral fitting results for electronic spectral data for $(C_5Me_5)_2U[\eta^2\text{-}(N,N')\text{-tetrazolate}]_2$ (**7**), in toluene solution. The fit is comprised of a sum of Gaussian bands (dashed lines) using an unconstrained non-linear least squares fitting routine. The best fit illustrated also required two additional bands (shown, but without peaks labeled) to higher energy than illustrated in the figure that contributed a significant tail into the UV region.

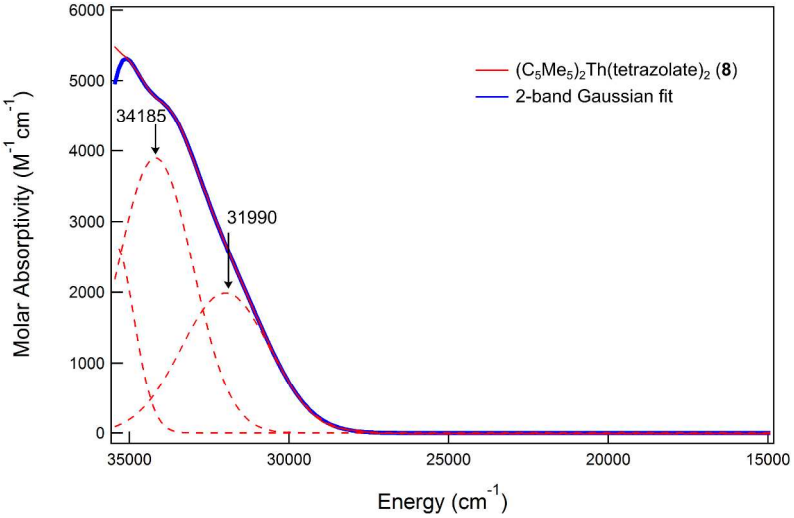


Figure S2. Spectral fitting results for electronic spectral data for $(C_5Me_5)_2Th[\eta^2\text{-}(N,N')\text{-tetrazolate}]_2$ (**8**), in toluene solution. The fit is comprised of a sum of Gaussian bands (dashed lines) using an unconstrained non-linear least squares fitting routine. The best fit illustrated also required one additional band (shown, but without peak labeled) to higher energy than illustrated in the figure that contributed a significant tail into the UV region.

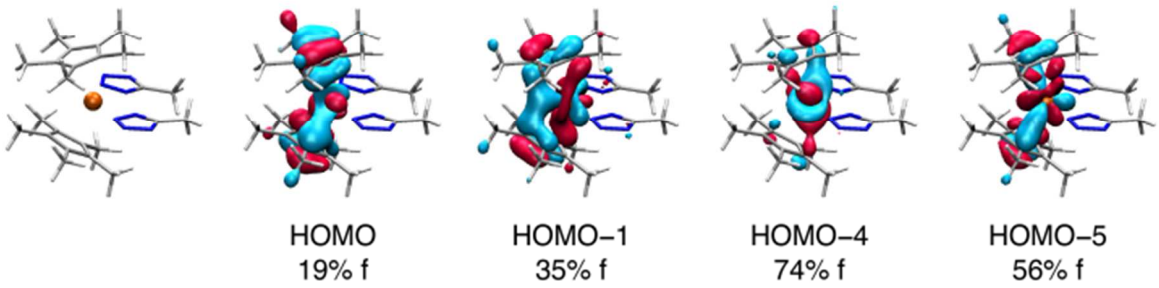


Figure S3. Molecular orbital pictures for $(C_5Me_5)_2U[\eta^2\text{-}(N,N')\text{-tetrazolate}]_2$ (**7**) of MOs with a significant contribution from the unpaired U 5f electrons.

Table S2. Molecular orbital energies for $(C_5Me_5)_2U[\eta^2\text{-}(N,N')\text{-tetrazolate}]_2$ (**7**) (relative to the HOMO of the α manifold) and $(C_5Me_5)_2Th[\eta^2\text{-}(N,N')\text{-tetrazolate}]_2$ (**8**) and percentage contributions from An f and d orbitals.

Molecular orbitals for the α manifold of $(C_5Me_5)_2U[\eta^2\text{-}(N,N')\text{-tetrazolate}]_2$ (**7**)

MO #	energy relative to HOMO [eV]	percentage contribution from U d orbitals	percentage contribution from U f orbitals
HOMO + 11	6.171	32	2
HOMO + 10	5.978	26	
HOMO + 9	5.849	28	16
HOMO + 8	5.543	10	
HOMO + 7	5.408	8	4
HOMO + 6	5.328	9	9
HOMO + 5	3.947	1	86
HOMO + 4	3.679	2	82
HOMO + 3	3.383	2	91
HOMO + 2	3.300	1	88
HOMO + 1	3.064	1	93
HOMO	0.000	2	19
HOMO – 1	−0.120	7	35
HOMO – 2	−0.276	5	21
HOMO – 3	−0.316	7	10
HOMO – 4	−0.430	1	74
HOMO – 5	−0.658	4	56
HOMO – 6	−1.846		
HOMO – 7	−1.882		
HOMO – 8	−1.889		
HOMO – 9	−1.922		4
HOMO – 10	−2.255		
HOMO – 11	−2.521	4	
HOMO – 12	−2.682		
HOMO – 13	−2.712	6	
HOMO – 14	−2.977	4	
HOMO – 15	−3.351		
HOMO – 16	−3.397		
HOMO – 17	−3.415		
HOMO – 18	−3.448		
HOMO – 19	−3.545	2	6
HOMO − 20	−3.584	4	
HOMO − 21	−3.956	5	1

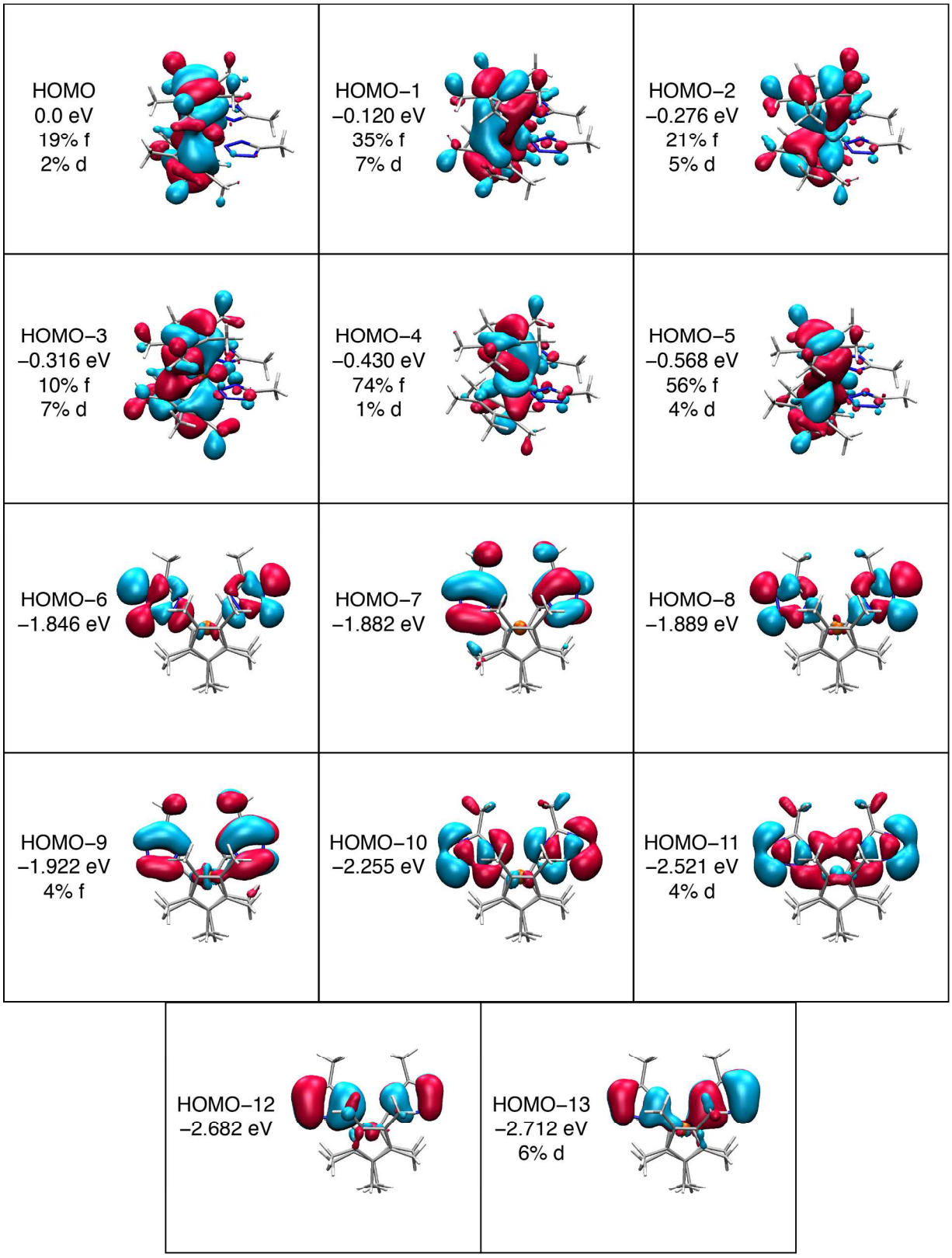
Molecular orbitals for the β manifold of $(C_5Me_5)_2U[\eta^2\text{-}(N,N')\text{-tetrazolate}]_2$ (**7**)

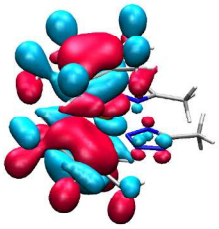
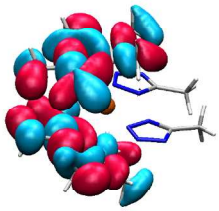
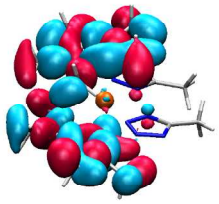
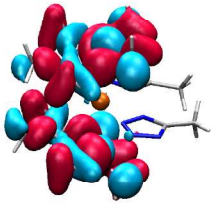
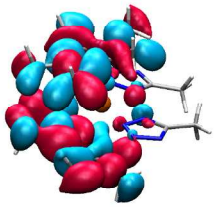
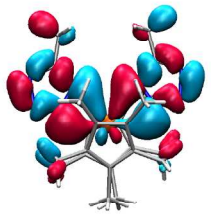
MO #	energy relative to HOMO [eV]	percentage contribution from U d orbitals	percentage contribution from U f orbitals
HOMO + 12	6.185	11	4
HOMO + 11	6.078	29	22
HOMO + 10	5.652	8	28
HOMO + 9	5.571	7	
HOMO + 8	5.447	8	5
HOMO + 7	4.658		90
HOMO + 6	4.553	3	80
HOMO + 5	4.460		85
HOMO + 4	4.222	2	72
HOMO + 3	4.111		86
HOMO + 2	4.072	1	88
HOMO + 1	4.018	2	88
HOMO	−0.024	1	7
HOMO – 1	−0.227	6	7
HOMO – 2	−0.237	5	1
HOMO – 3	−0.357	9	2
HOMO – 4	−1.839		
HOMO – 5	−1.882		
HOMO – 6	−1.891		
HOMO – 7	−2.247		
HOMO – 8	−2.514		
HOMO – 9	−2.667	4	
HOMO – 10	−2.694		1
HOMO – 11	−2.977	5	
HOMO – 12	−3.528	3	
HOMO – 13	−3.584		
HOMO – 14	−3.933		

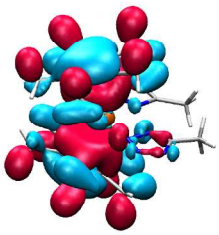
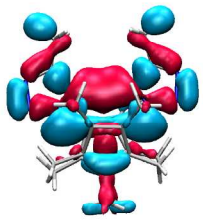
Molecular orbitals for $(C_5Me_5)_2Th[\eta^2\text{-}(N,N')\text{-tetrazolate}]_2$ (**8**)

MO #	energy relative to HOMO [eV]	percentage contribution from Th d orbitals	percentage contribution from Th f orbitals
HOMO + 10	6.042		48
HOMO + 9	5.760		88
HOMO + 8	5.741	6	14
HOMO + 7	5.515		19
HOMO + 6	5.232	7	64
HOMO + 5	5.019		71
HOMO + 4	4.909	6	69
HOMO + 3	4.654	11	57
HOMO + 2	4.593	20	52
HOMO + 1	4.524	8	46
HOMO	0.000		5
HOMO – 1	−0.210	7	
HOMO – 2	−0.275	8	5
HOMO – 3	−0.442	12	
HOMO – 4	−1.767		
HOMO – 5	−1.786		
HOMO – 6	−1.811		
HOMO – 7	−1.862		
HOMO – 8	−2.271		
HOMO – 9	−2.523		
HOMO – 10	−2.635		
HOMO – 11	−2.718	3	
HOMO – 12	−3.038	4	
HOMO – 13	−3.397		
HOMO – 14	−3.427		
HOMO – 15	−3.433		
HOMO – 16	−3.487		
HOMO – 17	−3.544		4
HOMO – 18	−3.593	4	
HOMO – 19	−3.965	8	

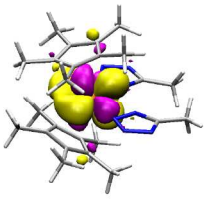
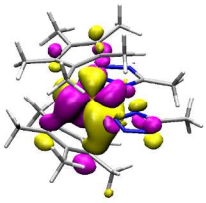
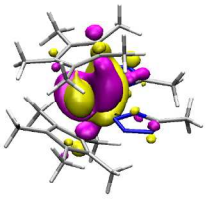
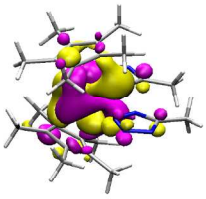
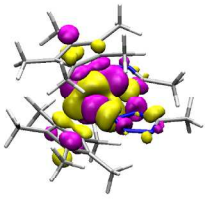
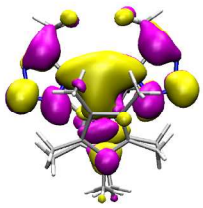
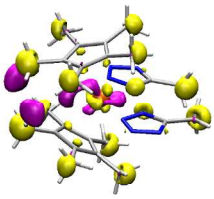
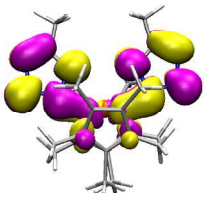
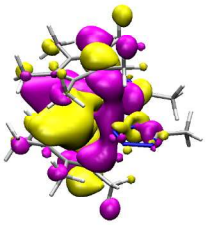
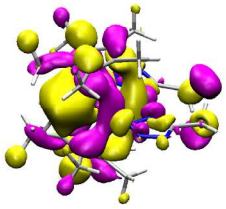
Figure S4. Pictures of the calculated orbitals (including virtual orbitals) for the α manifold for $(C_5Me_5)_2U[\eta^2\text{-}(N,N')\text{-tetrazolate}]_2$ (**7**)



HOMO−14 −2.977 eV 4%d 	HOMO−15 −3.351 eV 	HOMO−16 −3.397 eV 
HOMO−17 −3.415 eV 	HOMO−18 −3.448 eV 	HOMO−19 −3.545 eV 6% f 2% d 

HOMO−20 −3.584 eV 4% d 	HOMO−21 −3.956 eV 1% f 5% d 

Virtual Orbitals for the α manifold for $(C_5Me_5)_2U[\eta^2\text{-}(N,N')\text{-tetrazolate}]_2$ (**7**)

HOMO+1 3.064 eV 93% f 1% d 	HOMO+2 3.300 eV 88% f 1% d 	HOMO+3 3.383 eV 91% f 2% d 
HOMO+4 3.679 eV 82% f 2% d 	HOMO+5 3.947 eV 86% f 1% d 	HOMO+6 5.328 eV 9% f 9% d 
HOMO+7 5.408 eV 4% f 8% d 	HOMO+8 5.543 eV 10% d 	HOMO+9 5.849 eV 16% f 28% d 
HOMO+10 5.978 eV 26% d 	HOMO+11 6.171 eV 2% f 32% d