SUPPORTING INFORMATION

Assignment of the Oxidation States of Zr and Co in a Highly Reactive Heterobimetallic Zr/Co Complex Using X-ray Absorption Spectroscopy (XANES)

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CONTENTS

Table S1. Pre-edge energies at the Co K-edge for compounds in Co oxidation states ranging from +3 to -1, including additional commercial reference compounds not listed in Table 1.

Sample	Oxidation state	Pre-edge energy (eV)
$Co(NH_3)_6Cl_3$	3	7709.7
$LiCoO_2$	3	7709.7
$Co(acac)_3$	3	7709.8
$Co(acac)_2$	2	7709.3
$Co(acetate)_2$	2	7709.3
$CoCl_2$	2	7709.2
CoF_2	2	7709.2
$ClCo(PPh_3)_3$	1	7708.4
$ClZr(MesNP^iPr_2)_3CoI$ (**3**)	1	7708.4
$(^iPrNHPPh_2)_3CoI$ (**4**)	1	7708.0
$HOZr(MesNP^iPr_2)_3CoCO$ (**5**)	0	7707.8
$[Co(CO)_4]Na$	-1	No peak
$(THF)Zr(MesNP^iPr_2)_3CoN_2$ (**1**)	-1	No peak

Figure S1. Solid state XANES Co K-edge spectra from 7680.0 eV to 7760.0 eV of complex **1** and the Co^{-I} complex $Na[Co(CO)_4]$.

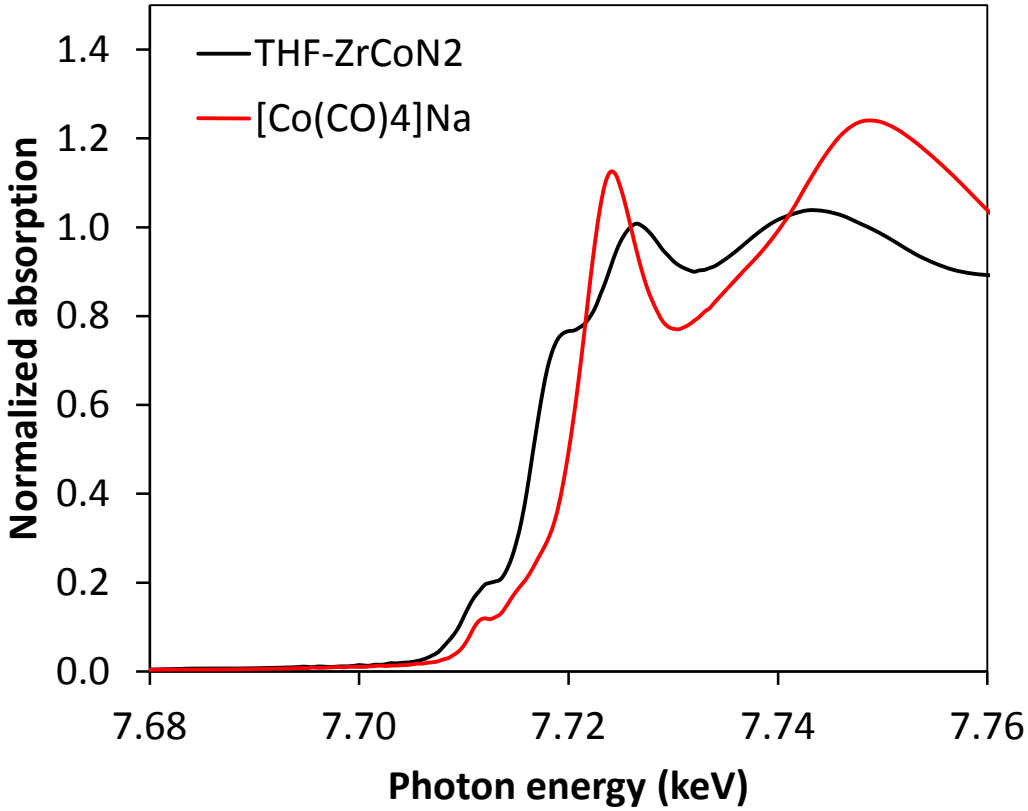


Figure S2. Solid state XANES Co K-edge spectra from 7680.0 eV to 7760.0 eV of complex **1** and the Co^{III} complex $Co(acac)_3$ (acac = acetylacetonate). The Co^{III} reference has a pre-edge feature at 7709.8 eV, while the pre-edge feature of **1** is absent (the small shoulder observed in this region is the leading edge of the XANES and not a pre-edge feature). The significantly higher energy of the edge of $Co(acac)_3$ is indicative of a higher oxidation state, as would be expected.

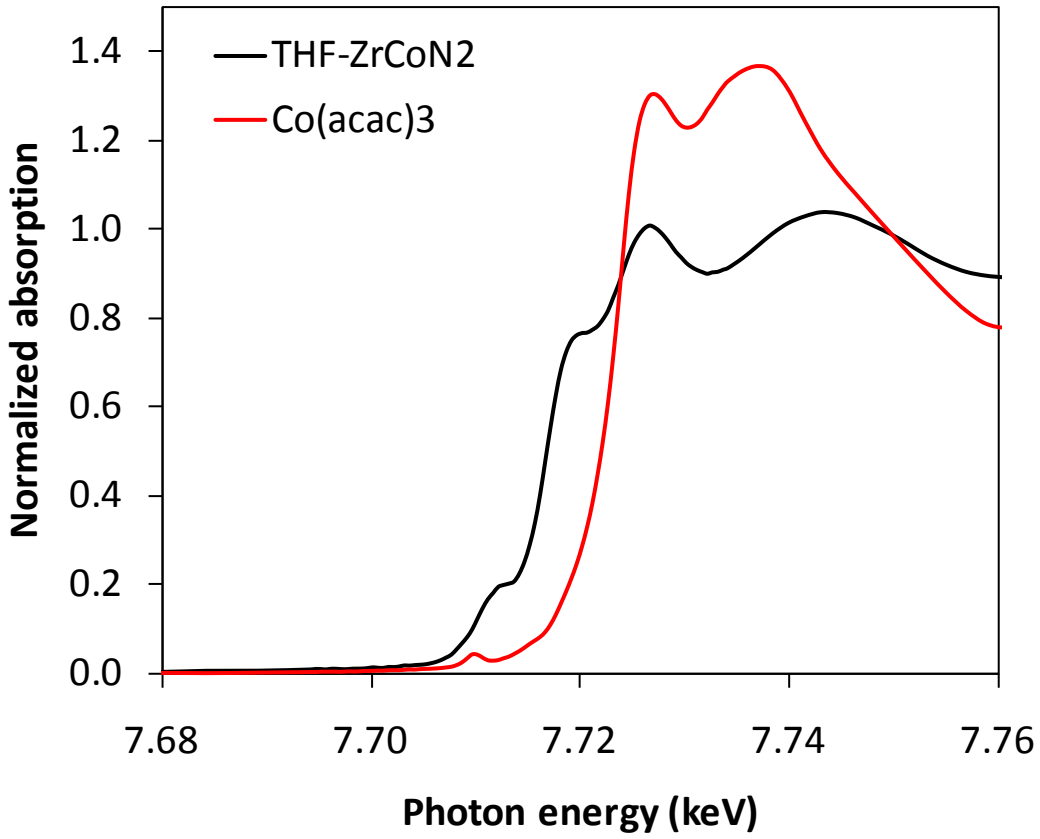


Figure S3. Solid state XANES Co K-edge spectrum from 7680.0 eV to 7760.0 eV of complex **1** (blue) and its first derivative (red). The position of the edge energy is denoted by a vertical dotted line.

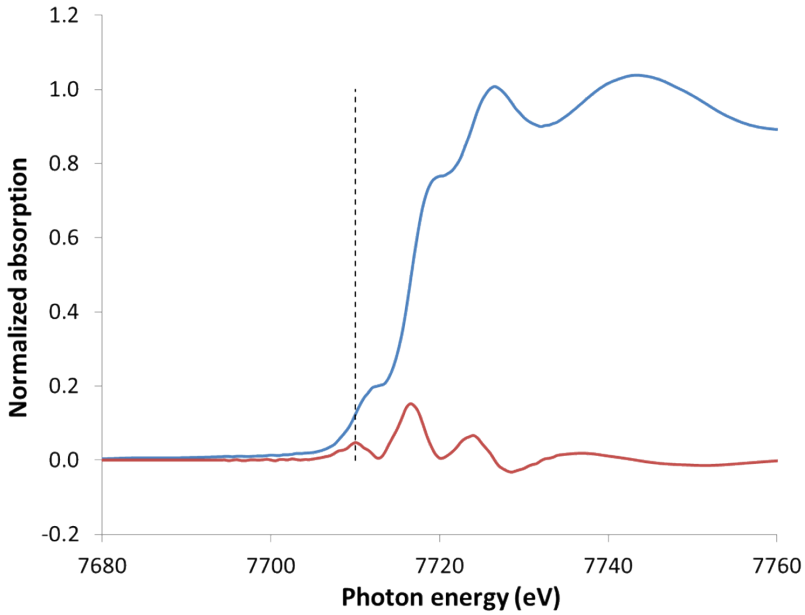


Figure S4. Solid state XANES Co K-edge spectrum from 7680.0 eV to 7760.0 eV of complex **3** (blue) and its first derivative (red). The position of the edge energy and the pre-edge energy are denoted by vertical dotted lines.

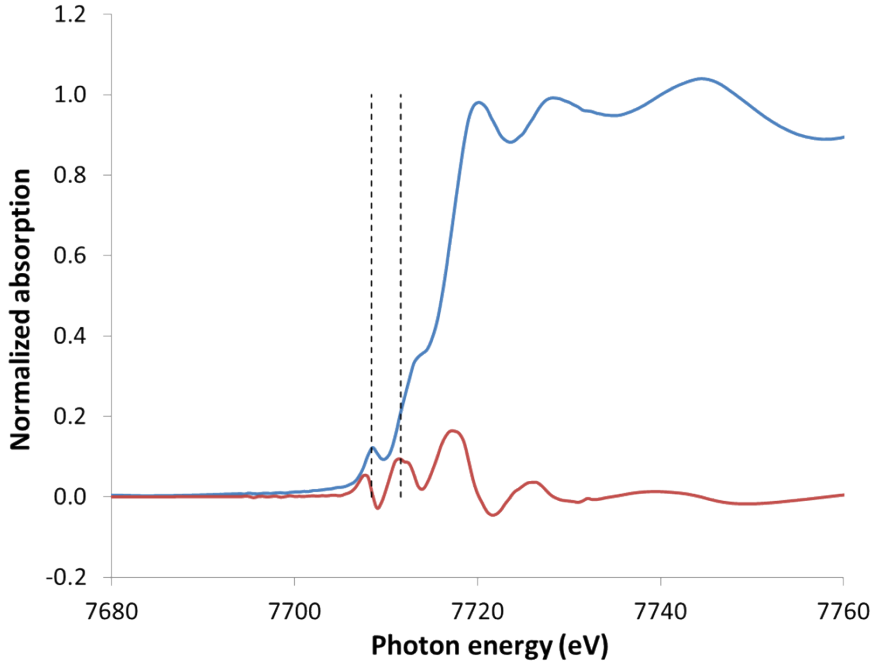


Figure S5. Solid state XANES Co K-edge spectrum from 7680.0 eV to 7760.0 eV of complex **4** (blue) and its first derivative (red). The position of the edge energy and the pre-edge energy are denoted by vertical dotted lines.

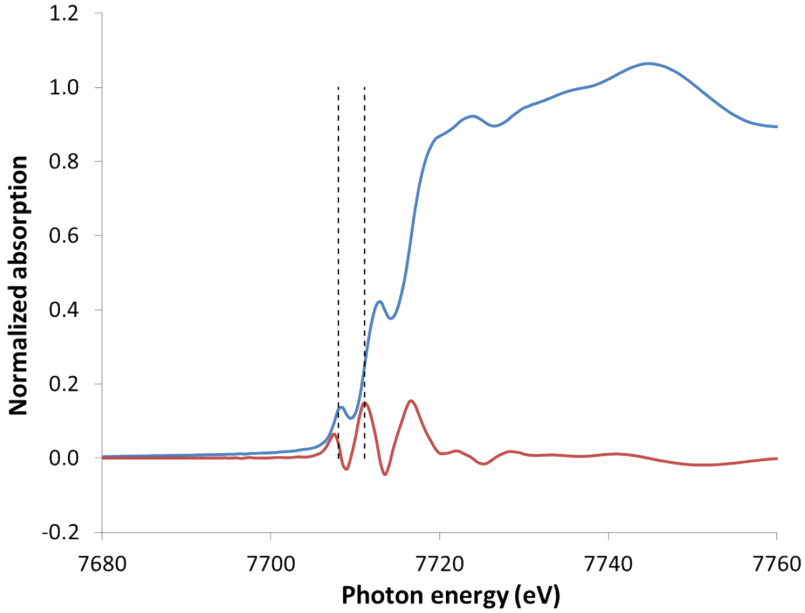


Figure S6. Solid state XANES Co K-edge spectrum from 7680.0 eV to 7760.0 eV of complex **5** (blue) and its first derivative (red). The position of the edge energy and the pre-edge energy are denoted by vertical dotted lines.

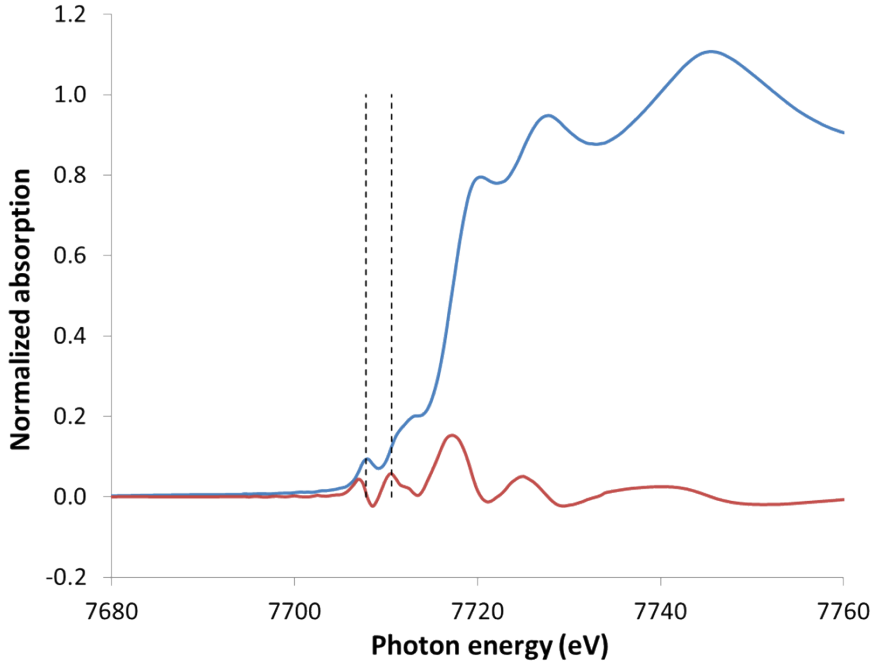


Figure S7. Solid state XANES Co K-edge spectrum from 7680.0 eV to 7760.0 eV of $Na[Co(CO)_4]$ (blue) and its first derivative (red). The position of the edge energy is denoted by a vertical dotted line.

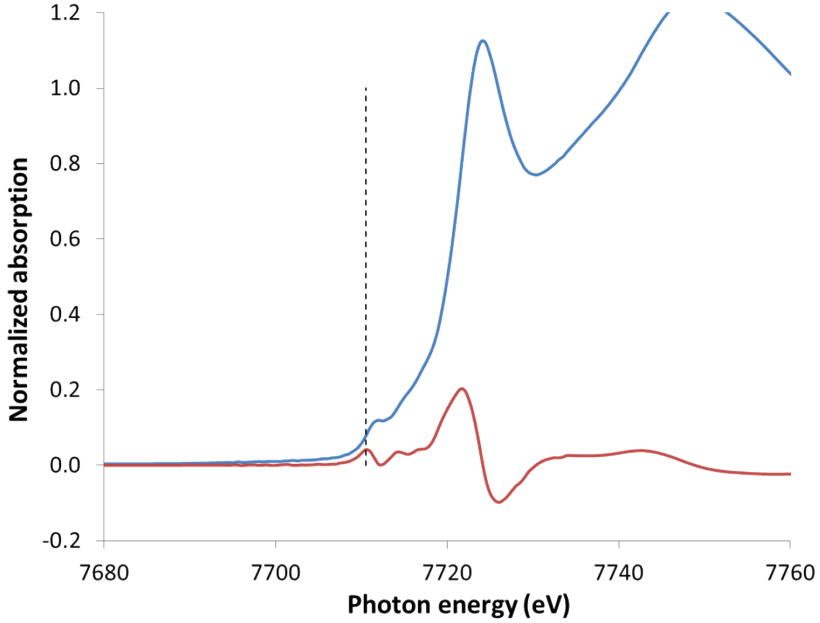


Figure S8. Solid state XANES Co K-edge spectrum from 7680.0 eV to 7760.0 eV of $ClCo(PPh_3)_3$ (blue) and its first derivative (red). The position of the edge energy is denoted by a vertical dotted line.

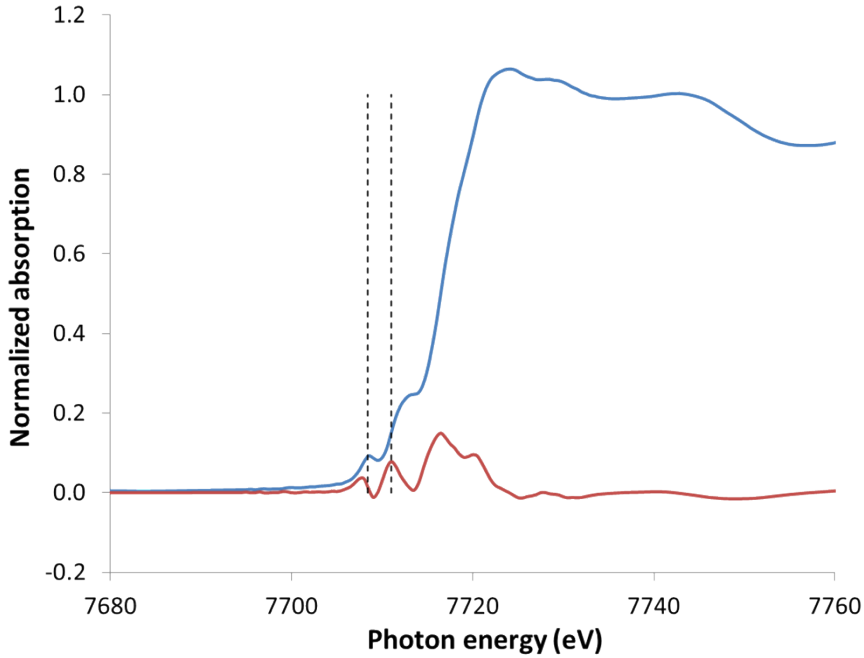


Figure S9. Solid state XANES Zr K-edge spectrum from 17960.0 eV to 18060.0 eV of complex **1** (blue) and its first derivative (red). The position of the edge energy is denoted by a vertical dotted line.

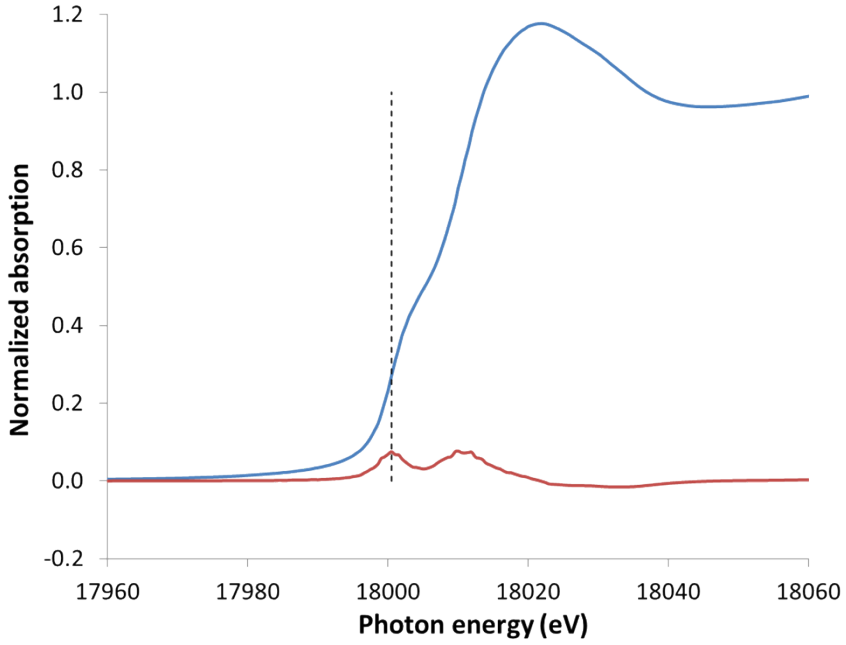


Figure S10. Solid state XANES Zr K-edge spectrum from 17960.0 eV to 18060.0 eV of complex **3** (blue) and its first derivative (red). The position of the edge energy is denoted by a vertical dotted line.

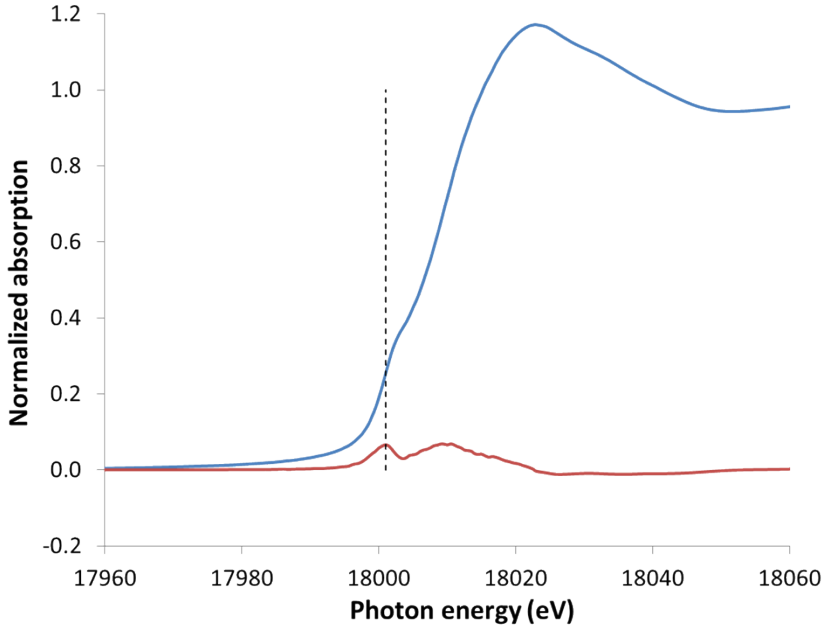


Figure S11. Solid state XANES Zr K-edge spectrum from 17960.0 eV to 18060.0 eV of complex **5** (blue) and its first derivative (red). The position of the edge energy is denoted by a vertical dotted line.

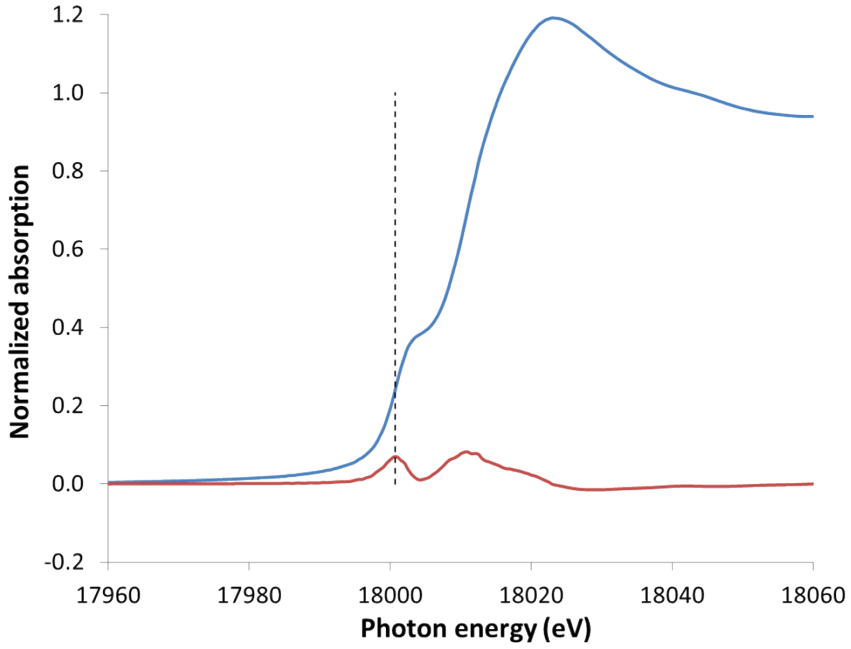
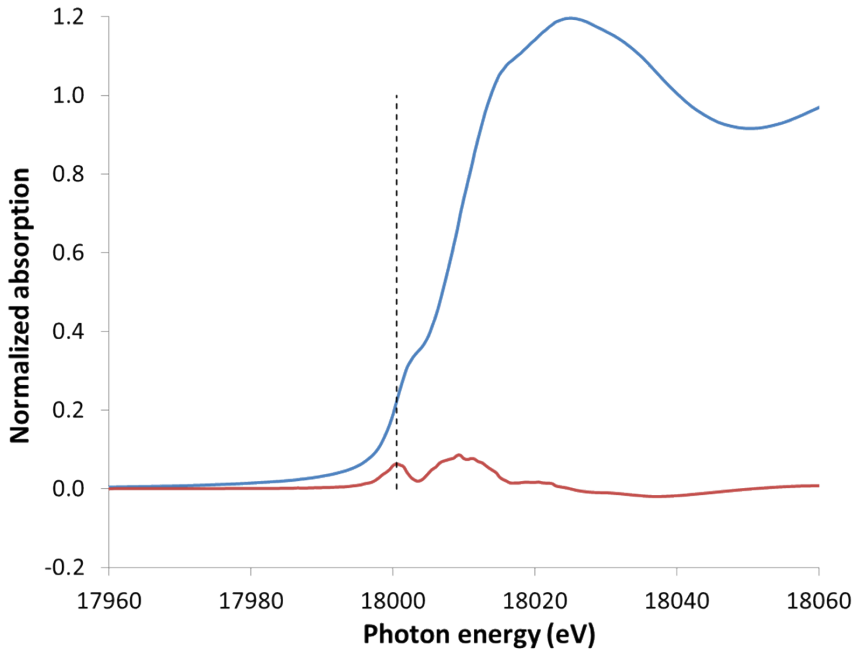


Figure S12. Solid state XANES Zr K-edge spectrum from 17960.0 eV to 18060.0 eV of complex **6** (blue) and its first derivative (red). The position of the edge energy is denoted by a vertical dotted line.



Gaussian 09 Full Reference

Gaussian 09, Revision **A.1**, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

Table S2. Comparison of selected interatomic distances derived from the DFT-optimized geometry and the experimentally determined geometry (X-ray crystallography) of **1**.[1]

	Computed (DFT-optimized)	**Experimental (X-ray)[1]**
Zr-Co	2.41 Å	2.36 Å
Zr-O	2.49 Å	2.46 Å
Zr-N (avg)	2.18 Å	2.15 Å
Co-P (avg)	2.26 Å	2.22 Å
Co-N	1.81 Å	1.83 Å

[1] Greenwood, B. P.; Rowe, G. T.; Chen, C.-H.; Foxman, B. M.; Thomas, C. M. *J. Am. Chem. Soc.* **2010**, *132*, 44-45.