We probe the dynamics of valence electrons in photoexcited [Fe(terpy)2]2+ in solution to gain deeper insight into the Fe ligand bond changes. We use hard X-ray emission spectroscopy (XES), which combines element specificity and high penetration with sensitivity to orbital structure, making it a powerful technique for molecular studies in a wide variety of environments. A picosecond-time-resolved measurement of the complete Is X-ray emission spectrum captures the transient photoinduced changes and includes the weak valence-to-core (vtc) emission lines that correspond to transitions from occupied valence orbitals to the nascent core-hole. Vtc-XES offers particular insight into the molecular orbitals directly involved in the light-driven dynamics; a change in the metal ligand orbital overlap results in an intensity reduction and a blue energy shift in agreement with our theoretical calculations and more subtle features at the highest energies reflect changes in the frontier orbital populations.