In liquid phase chemistry dynamic solute solvent interactions often govern the path, ultimate outcome, and efficiency of chemical reactions. These steps involve many-body movements on subpicosecond time scales and thus ultrafast structural tools capable of capturing both intramolecular electronic and structural changes, and local solvent structural changes are desired. We have studied the intra- and intermolecular dynamics of a model chromophore, aqueous [Fe(bpy)$_3$]$^{2+}$, with complementary X-ray tools in a single experiment exploiting intense XFEL radiation as a probe. We monitored the ultrafast structural rearrangement of the solute with X-ray emission spectroscopy, thus establishing time zero for the ensuing X-ray diffuse scattering analysis. The simultaneously recorded X-ray diffuse scattering patterns reveal slower subpicosecond dynamics triggered by the intramolecular structural dynamics of the photoexcited solute. By simultaneous combination of both methods only, we can extract new information about the solvation dynamic processes unfolding during the first picosecond (ps). The measured bulk solvent density increase of 0.2% indicates a dramatic change of the solvation shell around each photoexcited solute, confirming previous ab initio molecular dynamics simulations. Structural changes in the aqueous solvent associated with density and temperature changes occur with similar to 1 ps time constants, characteristic for structural dynamics in water. This slower time scale of the solvent response allows us to directly observe the structure of the excited solute molecules well before the solvent contributions become dominant.