Photon-Mediated Hybridization of Molecular Vibrational States

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Supplementary Information

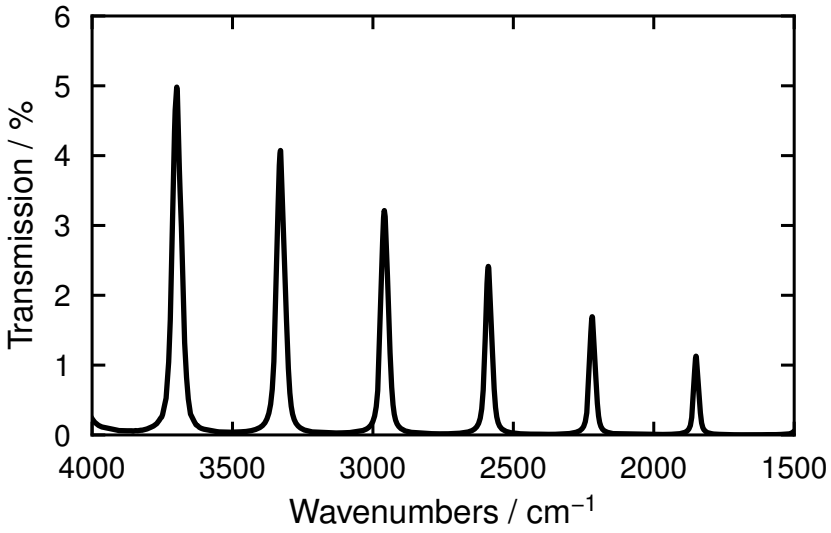

Figure S1: FTIR transmission spectrum of the empty microfluidic Fabry–Pérot cavity. The spacing between the windows was controlled with Mylar film to $\approx 11\,\mu m$ such that the $n = 6$ optical state of the cavity overlapped in energy with both vibrational states of the molecules. This resulted in cavity modes with a $30\,cm^{-1}$ bandwidth. The changing intensity of the peaks is due to the changing optical constants of Au in this region.

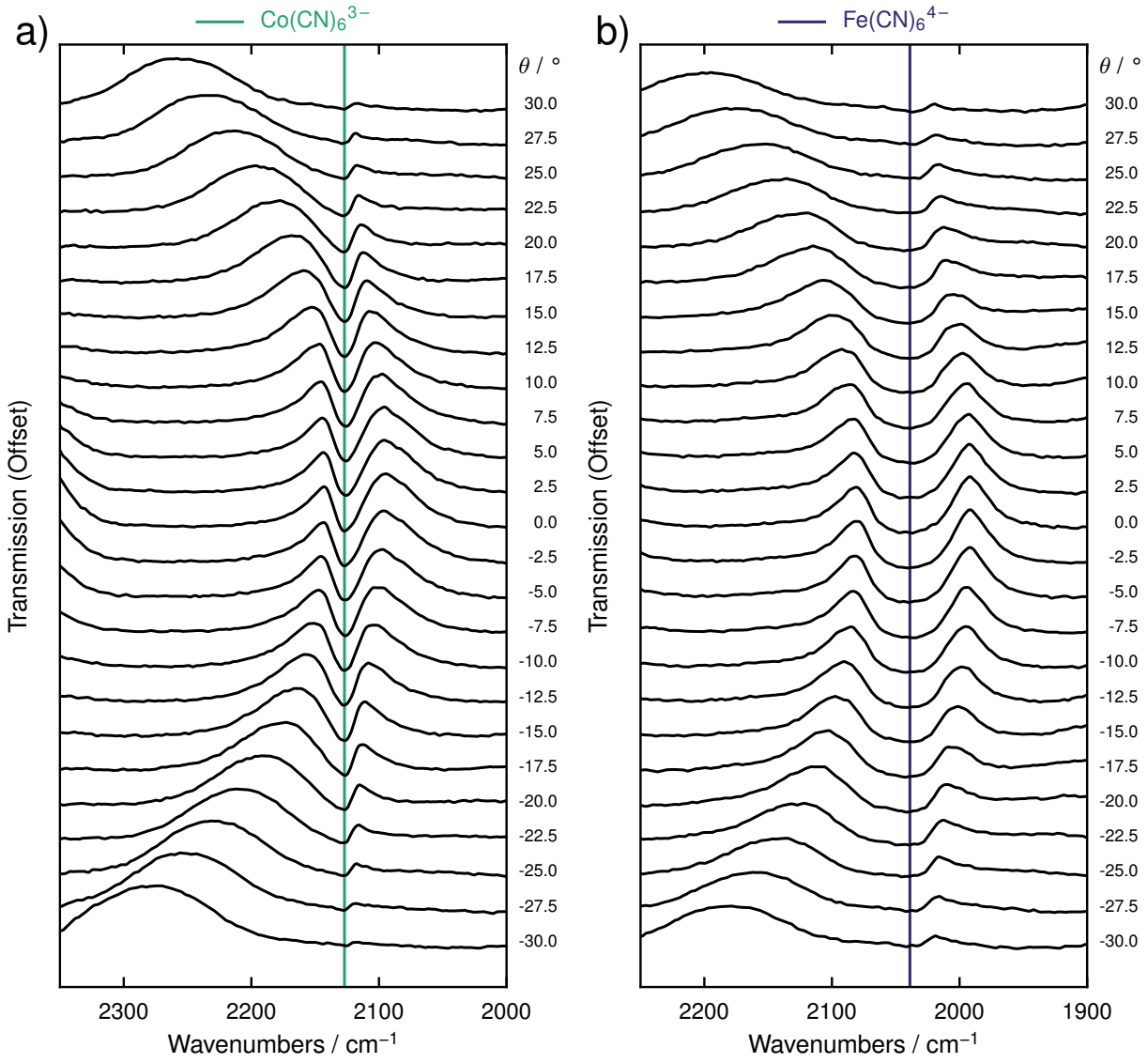

Figure S2: Transmission spectra of (a) 0.379 M $Co(CN)_6^{3-}$ and (b) 0.379 M $Fe(CN)_6^{4-}$ solutions strongly coupled to the optical mode as a function of incidence angle, θ. The green and navy vertical lines are the locations of the $Co(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ molecular resonances, respectively. In both experiments, the two peaks are associated with the upper and lower polaritons, whose positions are determined as a function of angle for the fitting shown in Figure 3.

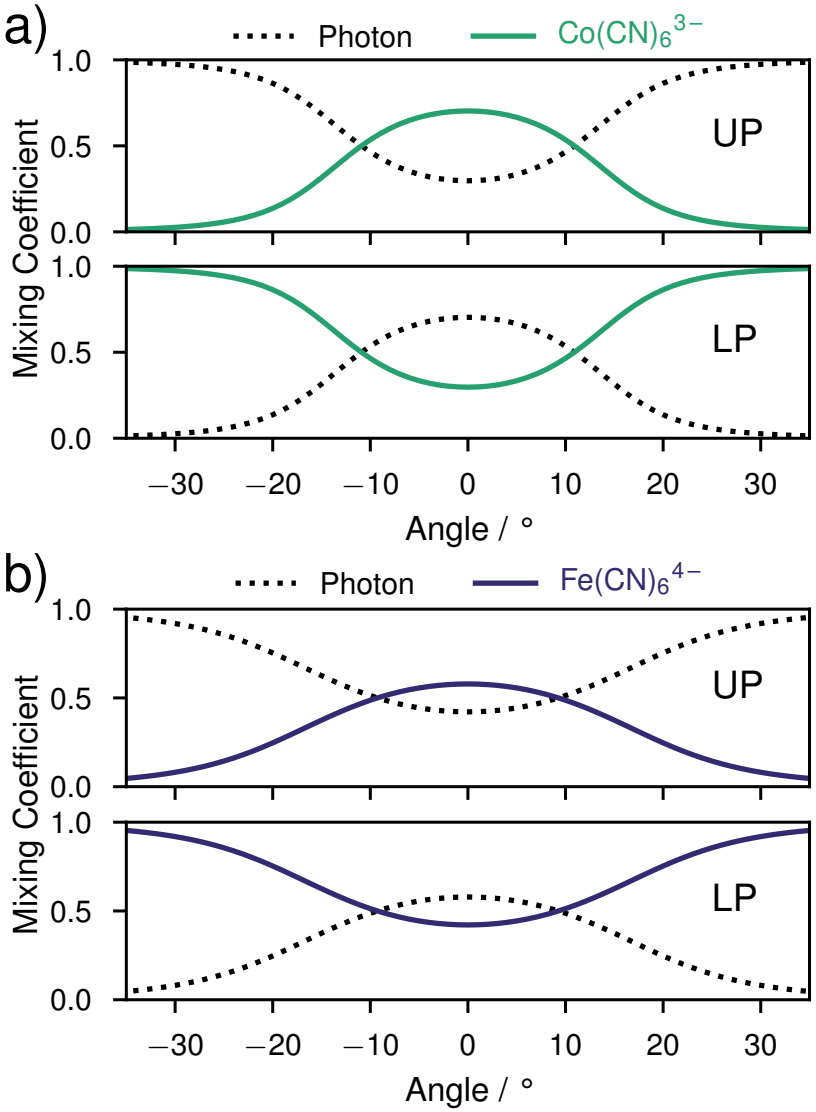

Figure S3: Polariton mixing coefficients, $|\alpha|^2$ and $|\beta|^2$, from fitting experimental data from Figure 3/S2 to Equation 5 for the UP and LP branches for (a) 0.379 M $K_3[Co(CN)_6]$, (b) 0.379 M $K_4[Fe(CN)_6]$. At an angle $\theta \approx \pm 10°$, $|\alpha|^2 = |\beta|^2 = 0.5$ for both solutions, and the optical and molecular states contribute equally to both of the polariton states. At larger angles, the dispersive UP branch has mostly optical character, while the LP branch is mainly molecular.

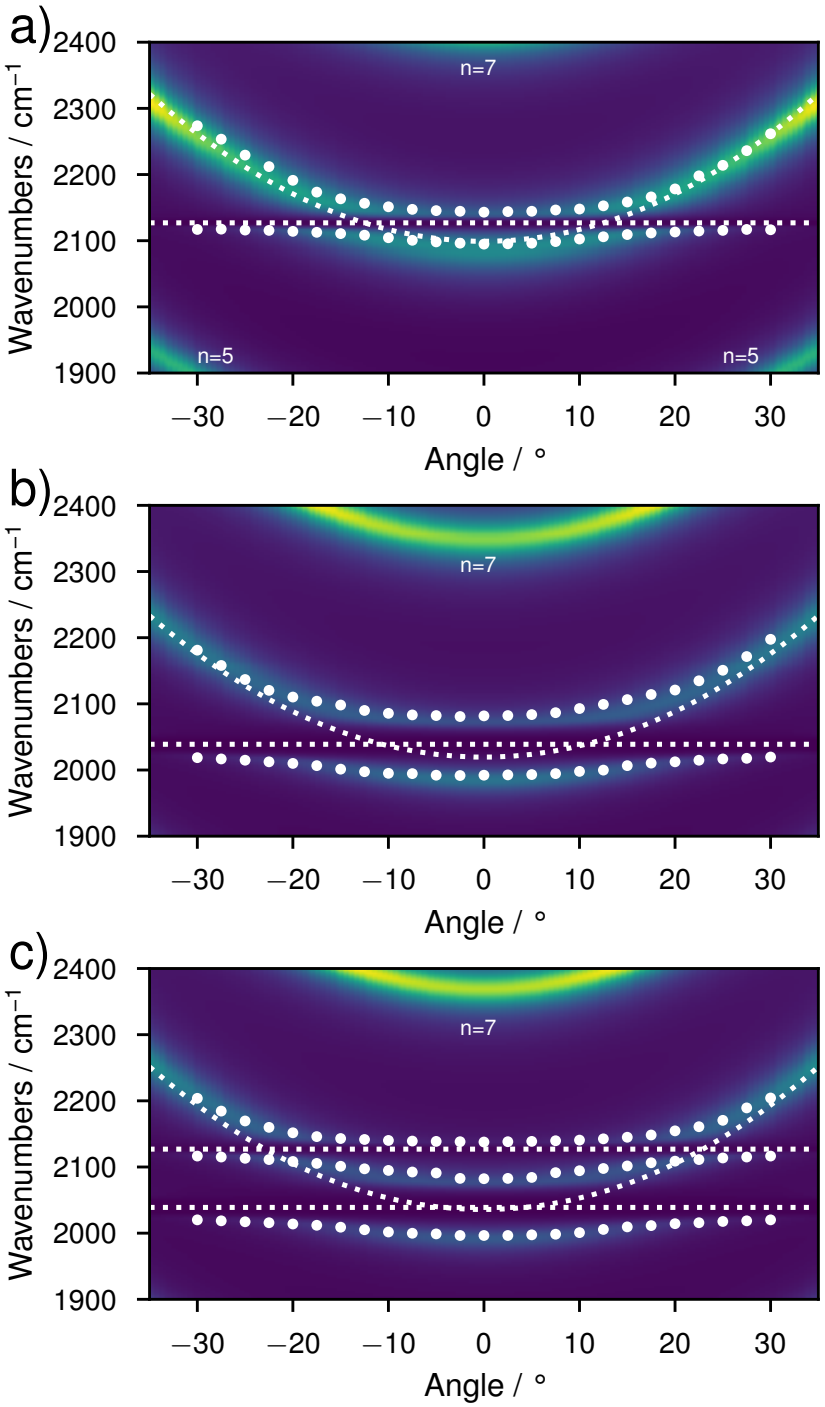

Figure S4: Experimentally determined polariton peak positions (white circles) overlaid onto 2D colormap transfer matrix calculations of angular dispersion for (a) 0.379 M $K_3[Co(CN)_6]$, (b) 0.379 M $K_4[Fe(CN)_6]$ (c) 0.379 M $K_3[Co(CN)_6]$ / 0.379 M $K_4[Fe(CN)_6]$ solutions. The dashed white lines are the peak positions of the uncoupled cavity modes (curves) and the fixed position of the molecular resonances (horizontal lines). Additionally, uncoupled optical modes ($n = 5$ and $n = 7$) are labeled in each plot.