Supporting Information: Fano description of single-hydrocarbon fluorescence excited by a scanning tunneling microscope

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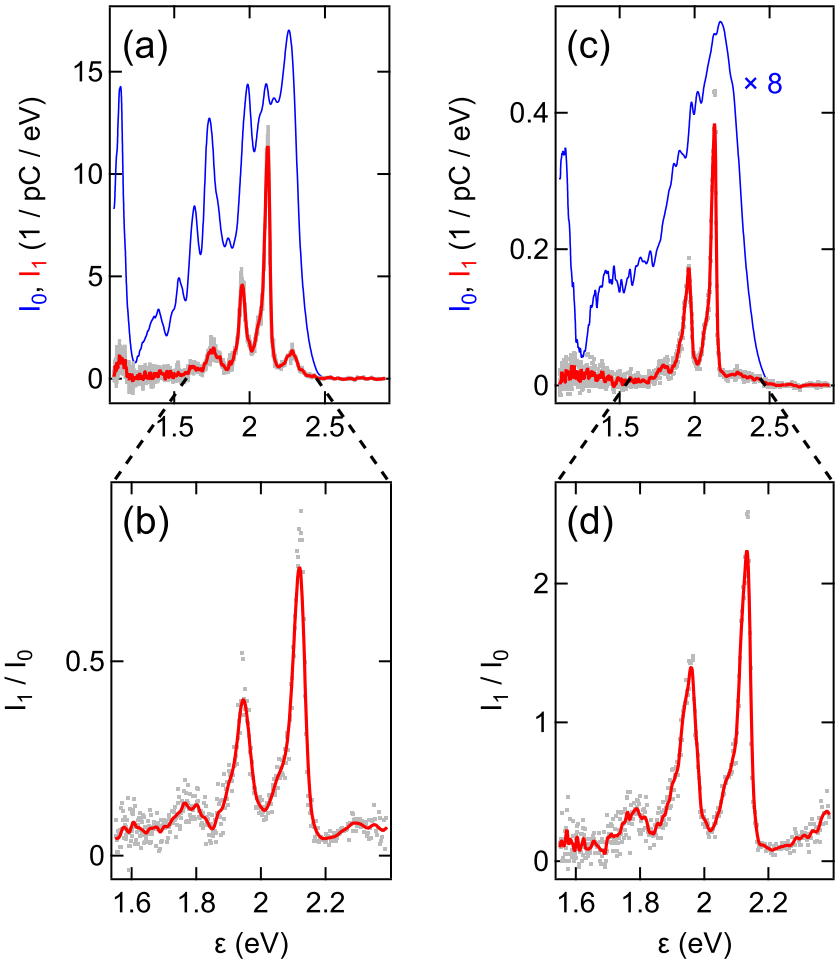

Figure S1: (a) Fluorescence spectrum (I_1) of Fig. 1(f) in the main manuscript. The superimposed thin blue line is the spectral profile of the tip-induced plasmon (I_0, -2.5 V, 300 pA, 60 s) acquired on a 3-layer NaCl island sufficiently far away from DBP molecules. It exhibits a maximum at photon energy $\varepsilon = 2.26$ eV, which is close to a maximum of the molecular fluorescence spectrum at 2.28 eV. (b) Molecular fluorescence spectrum divided by the plasmon line shape, I_1/I_0. A weak contribution at 2.28 eV is still discernible. (c) Luminescence spectrum (I_1) of Fig. 2 (top) in the main manuscript. The line shape of plasmonic luminescence (I_0, -2.5 V, 300 pA, 120 s) is added as a thin blue line. In contrast to (a), a fluorescence peak at 2.28 eV is not visible, neither in the raw nor in the normalized data of panel (d). (d) Normalized molecular fluorescence spectrum, I_1/I_0.

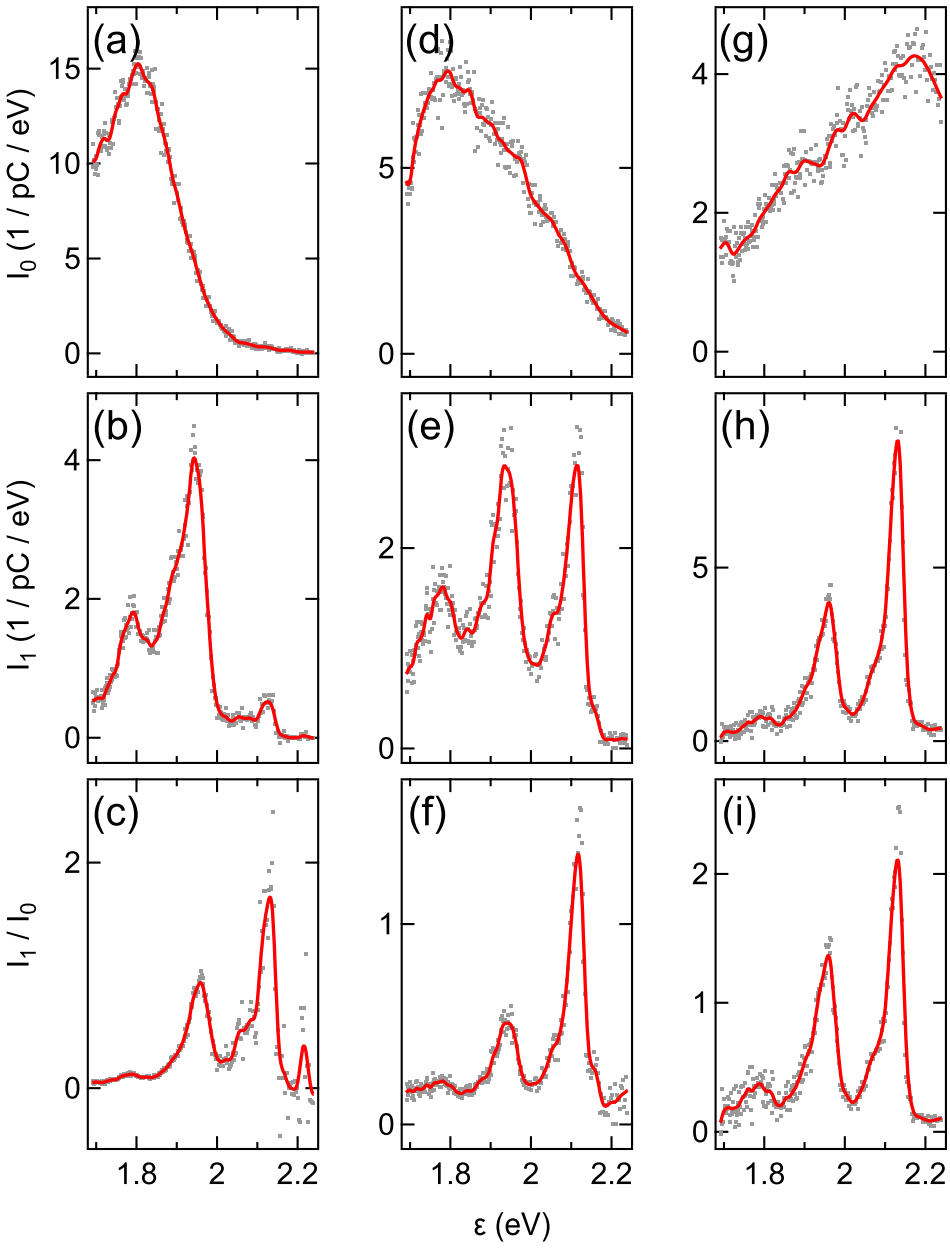

Figure S2: Normalization of raw single-DBP fluorescence spectra by the plasmon luminescence spectra. (a) Luminescence spectrum of tip-induced plasmon, I_0, acquired atop a 3-layer NaCl island on Ag(111) (-2.5 V, 300 pA, 120 s). (b) Fluorescence spectrum of DBP, I_1, adsorbed on a 3-layer NaCl island on Ag(111) (-2.5 V, 300 pA, 180 s). (c) Normalized DBP luminescence spectrum, I_1/I_0. (d) — (f), (g) — (i) Like (a) — (c) for different tip-induced plasmons and DBP molecules on 3-layer NaCl islands.

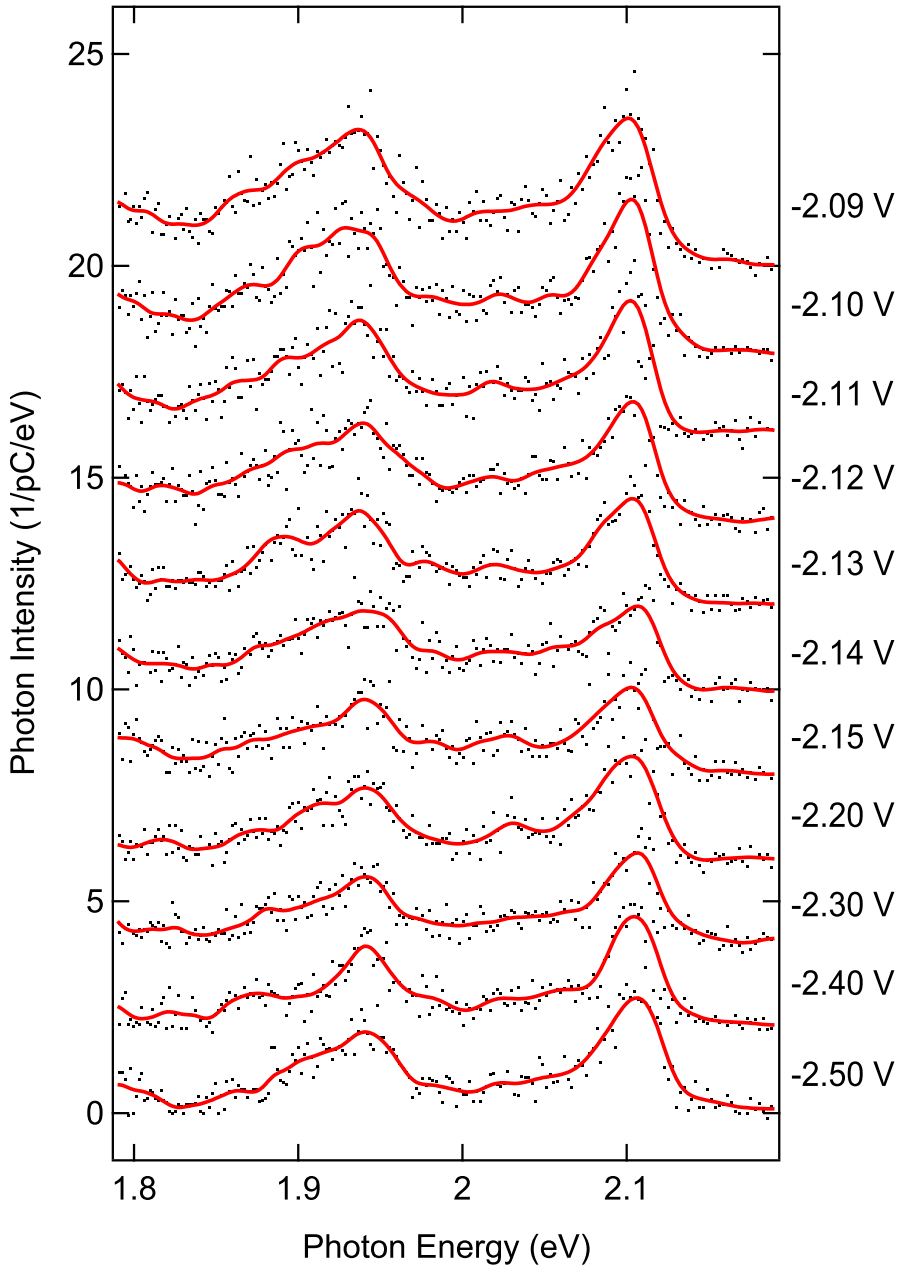

Figure S3: Evolution of DBP fluorescence spectra with varying bias voltage. The light spectra were acquired with the tip atop DBP at the position indicated by an asterisk in Fig. 1(b). Spectra with voltages $\leq -2.20\,\mathrm{V}$ were recorded with 100 pA (120 s). For voltages $> -2.20\,\mathrm{V}$ the tunneling current was reduced to 50 pA and the acquisition time increased to 240 s. Instabilities of the junction for bias voltages $> -2.09\,\mathrm{V}$ hampered the reproducible recording of fluorescence spectra.

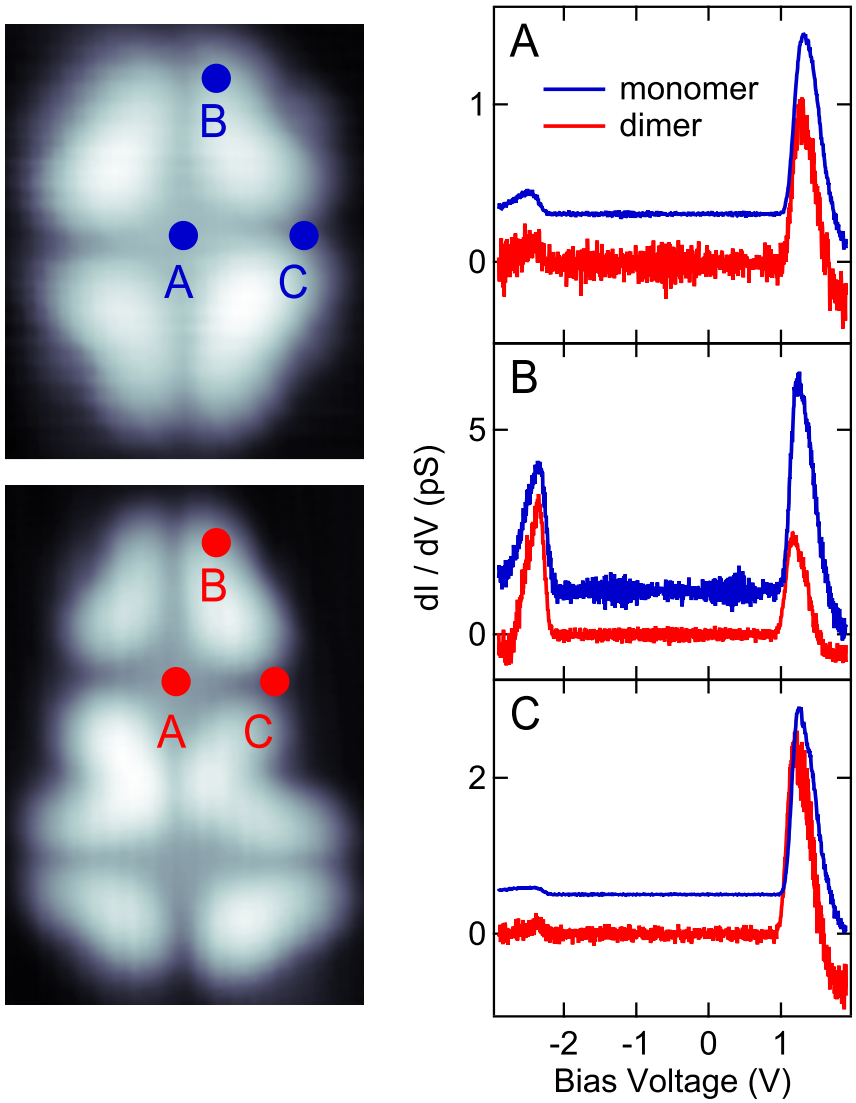

Figure S4: Comparison of constant-height $\mathrm{d}I/\mathrm{d}V$ spectra acquired atop positions A, B, C of a DBP monomer (blue) and dimer (red) on a 3-layer NaCl island on Ag(111) (feedback loop parameters: $-3\,\mathrm{V}$, $100\,\mathrm{pA}$). The monomer spectra are vertically offset for clarity. The STM images of the monomer (top left panel, $2.6 \times 3.5\,\mathrm{nm}^2$) and of the dimer (bottom left panel, $3.6 \times 4.4\,\mathrm{nm}^2$) were recorded at $-2.5\,\mathrm{V}$, $5\,\mathrm{pA}$.

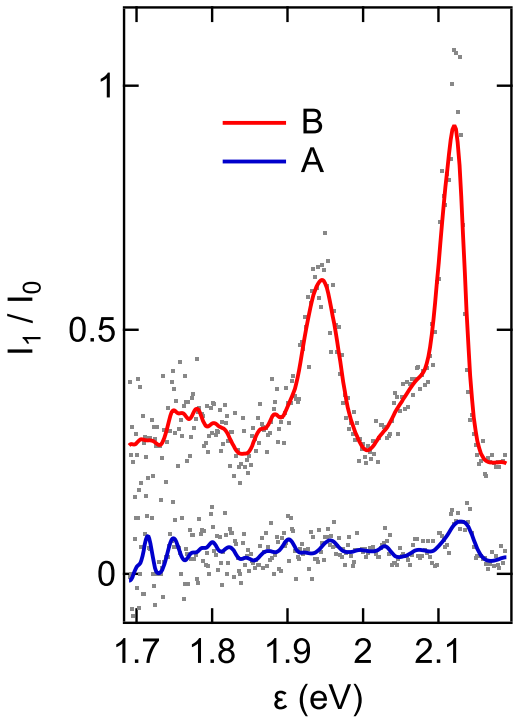

Figure S5: Normalized fluorescence spectra acquired atop positions A, B (Figure S3) on a DBP dimer adsorbed to a 3-layer NaCl island (−2.5 V, 300 pA, 60 s). Spectrum B is vertically offset.

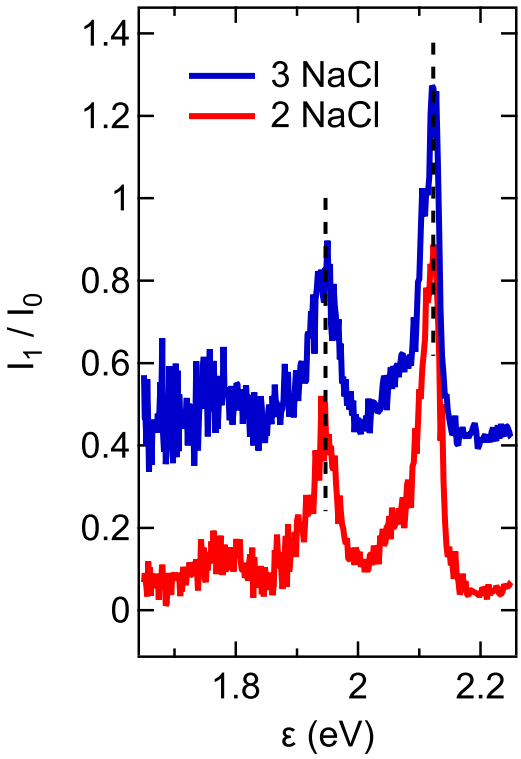

Figure S6: Normalized fluorescence spectra of a DBP dimer on 3-layer (top) and 2-layer NaCl islands on Ag(111) (−2.5 V, 300 pA, 60 s). Both spectra were acquired at position B indicated in Figure S3. The spectrum acquired atop DBP on 3-layer NaCl is vertically offset. Differences in the molecular luminescence on 3-layer and 2-layer NaCl are negligible. The dashed lines indicate the essentially invariant energy of photon emission peaks.

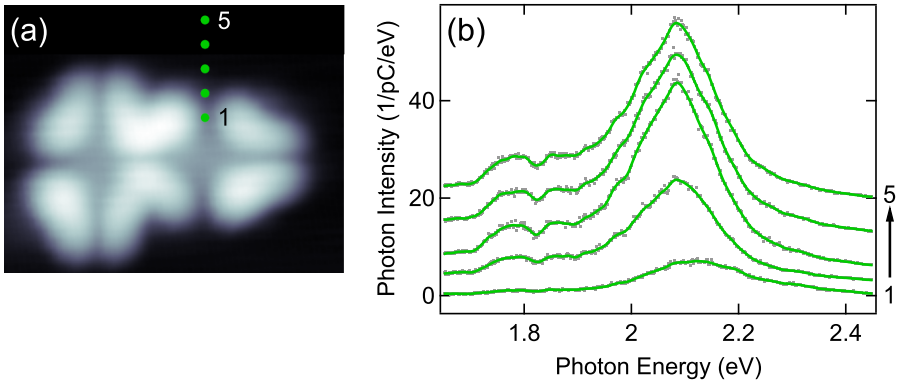

Figure S7: (a) STM image of a DBP dimer on a 2-layer NaCl island ($-2.5\,\mathrm{V}$, $10\,\mathrm{pA}$, $4.8 \times 4\,\mathrm{nm}^2$). (b) Luminescence spectra ($-2.5\,\mathrm{pA}$, $300\,\mathrm{pA}$, $180\,\mathrm{s}$) recorded along the line defined by the equidistantly ($0.375\,\mathrm{nm}$) arranged green markers in (a). Distance $d = 0\,\mathrm{nm}$ corresponds to the bottom marker in (a). The spectra are arranged from $d = 0\,\mathrm{nm}$ (bottom) to $d = 1.5\,\mathrm{nm}$ (top). Raw data appear as dots. The solid line represents smoothed data and serves as a guide to the eye. Inside the molecule (bottom spectrum) the sharp transition peaks of the molecule are suppressed. Rather, a broad feature with maximum at $\approx 2.11\,\mathrm{eV}$ is observed. Upon increasing the lateral tip–DBP separation the plasmon spectroscopic signature progressively gains intensity and exhibits a peak at $\approx 2.08\,\mathrm{eV}$.

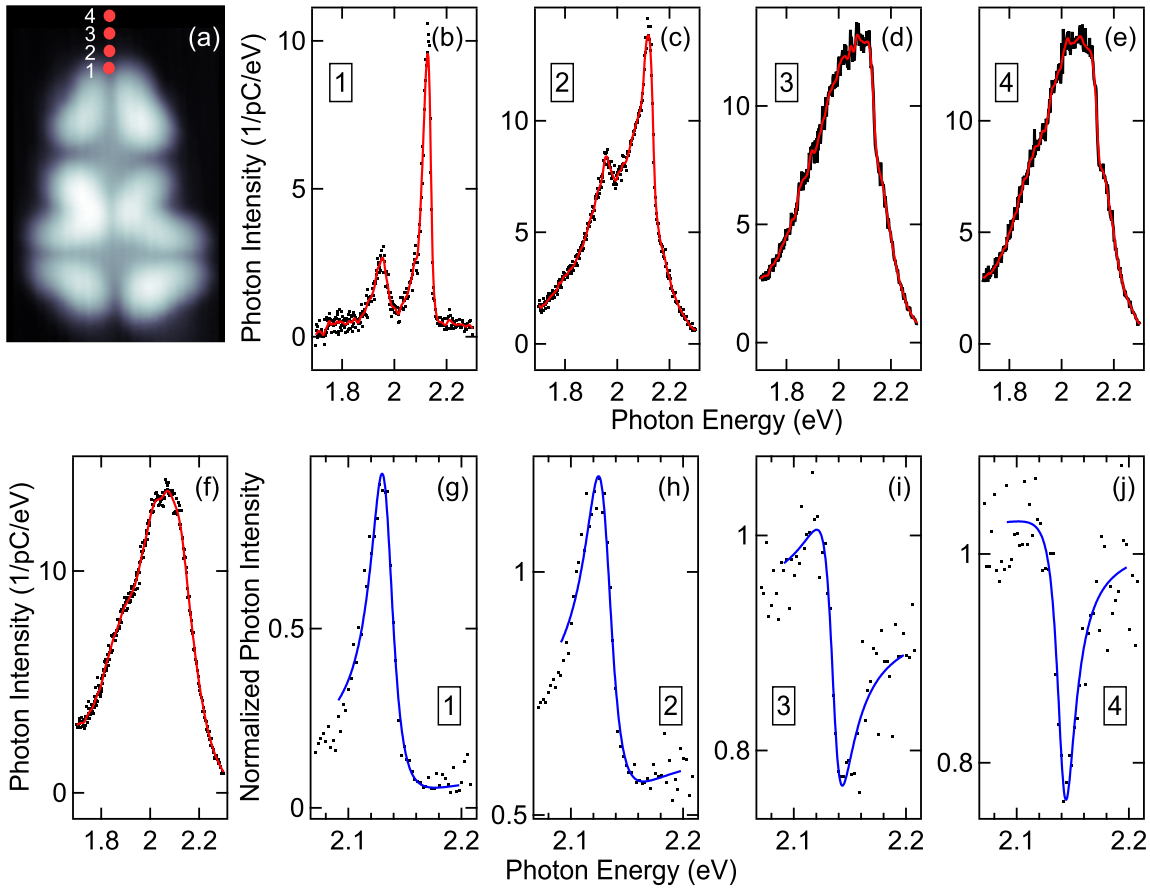

Figure S8: (a) STM image of a DBP dimer on 2-layer NaCl island (−2.5 V, 10 pA, 3.4 × 5.0 nm^2) with indicated positions (1–4) of fluorescence spectra. Distances are given with respect to position 1 of Fig. 3(a) of the main manuscript, *i. e.*, d = 0.1 nm (1), 0.4 nm (2), 0.7 nm (3), 1.0 nm (4). (b)–(e) Fluorescence spectra (dots) acquired at positions 1–4 indicated in (a). Spectrum 1 was acquired with parameters −2.5 V, 300 pA, 60 s, while spectra 2-4 were recorded at −2.5 V, 600 pA, 120 s. The solid lines represent smoothed data. (f) Luminescence spectrum (dots) on 2-layer NaCl several nm away from DBP molecules showing the light intensity due to the plasmon decay (−2.5 V, 600 pA, 120 s). The solid line represents smoothed data. (g)–(j) Normalized spectra in the photon energy region of the $S_1 \longrightarrow S_0$ transition peak. Each spectrum in (b)–(g) was divided by the smoothed plasmonic light line shape shown as a solid line in (f). The solid line is a Fano line shape fit to the normalized fluorescence data (dots). The fit parameters q, ε_0, Γ are included in Fig. S9 as squares.

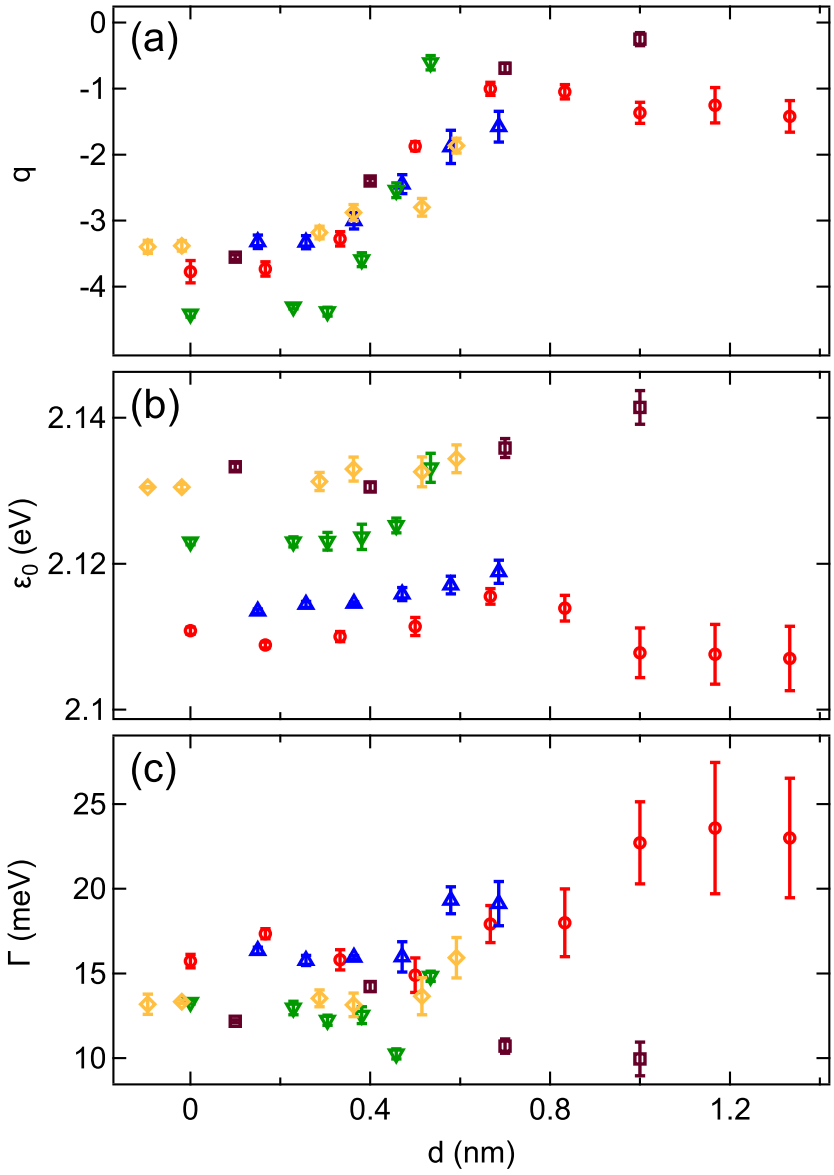

Figure S9: Distance dependence of Fano fit parameters (a) q, (b) ε_0, (c) Γ obtained for several DBP dimers on 2-layer NaCl islands. The circles indicate the data sets of the main manuscript. Distance $d = 0\,\mathrm{nm}$ is defined as the bottom data acquisition site along the vertical line depicted in Fig. 3(a) of the main text. A negative d reflects a position closer to the DBP center than the bottom acquisition site of Fig. 3(a). The uncertainty margins reveal the range of q, ε_0, Γ for which the Fano fit to experimental data is still reasonable.