Near-field radiative heat transfer between bodies separated by small, sub-wavelength gaps can exceed the bounds described by the famous Stefan–Boltzmann law by orders of magnitudes, bounded only by material dissipation and suitable choice of geometry. While typical transfer rates between uniform plates can already exceed blackbody limits, they are known to be highly suboptimal, motivating recent efforts to explore other geometries such as gratings and multilayer films which can in principle result in larger heat exchange. Here, we show that frequency-selective radiative heat transfer can be further enhanced between unconventional geometries discovered by application of large-scale optimization techniques. First, we explore structures optimized over one-dimensional degrees of freedom, showing that complicated, aperiodic multilayer slabs can allow realization of perfect rate-matching over a broader range of evanescent wavevectors, leading to a logarithmic enhancement factor compared to uniform media. Moreover, the flux between a dipolar particle and an optimized multilayer---proportional to the local density of states---is found to be orders of magnitude larger. Second, we employ adjoint shape optimization to discover grating geometries designed over two-dimensional degrees of freedom. We find that optimized gratings can allow realization of near-field resonances capable of achieving near-field rate-matching over the entire Brillouin zone, leading to approximately 100 times larger heat exchange compared to their bulk counterparts.