Supporting Information: Energy-based Plasmonicity Index to Characterize Optical Resonances in Nanostructures

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Robustness of the EPI on ϵ

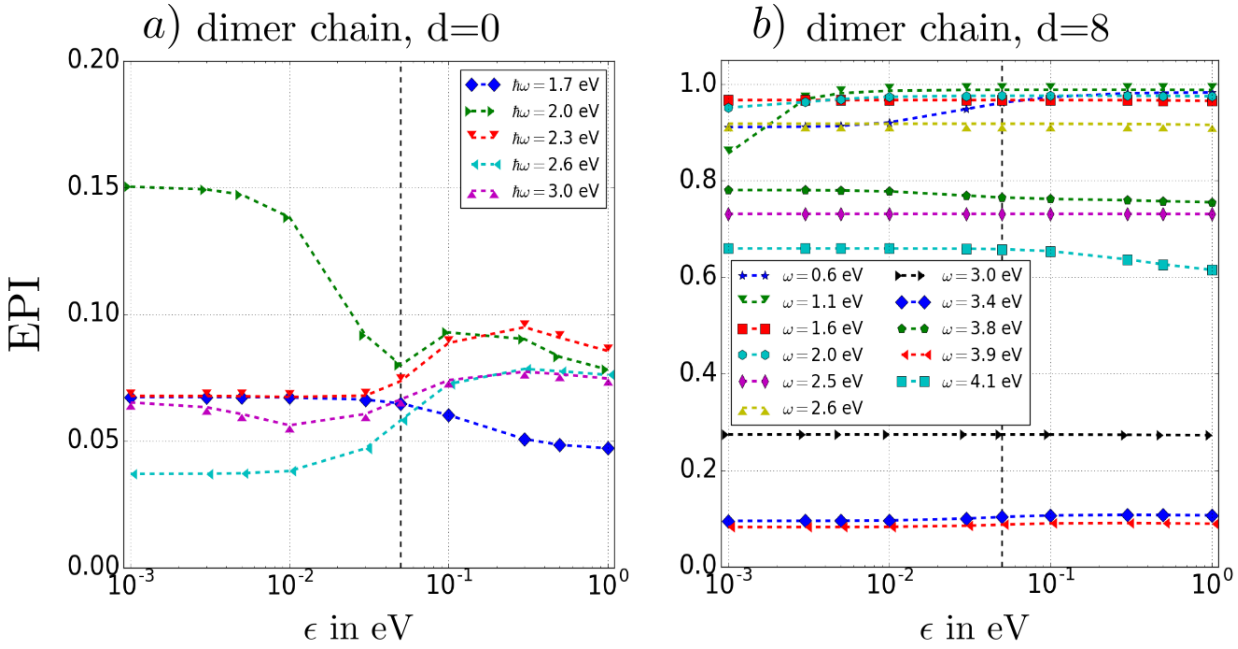

Figure S1: Energy-based plasmonicity index for the neutral (a) and 8-fold doped (b) dimer chains as a function of the broadening parameter ϵ. The vertical dashed line indicates the value $\epsilon = 0.05\,\mathrm{eV}$ used in the main body of the paper. The colored dashed lines serve as a guide to the eye to follow the individual resonances of the structure under consideration while ϵ is modified. Please note, that the horizontal axes are in log-scale and the vertical axis of the undoped dimer chain shows the range between 0 and 0.2 only, where all EPIs of the investigated resonances of the system are located.

Figure S1 shows the EPI of several resonances of the undoped (a) and the 8-fold doped (b) dimer chain as a function of the broadening parameter ϵ in Eqs. 7 and 8 of the main body of the paper. Please note, that the vertical axis in Fig. S1a ranges from 0 to 0.2 only and that the horizontal axes are in logarithmic scale. We can see that the EPI depends on the choice of ϵ only marginally. In particular, none of the investigated resonances changes its character as ϵ is modified.

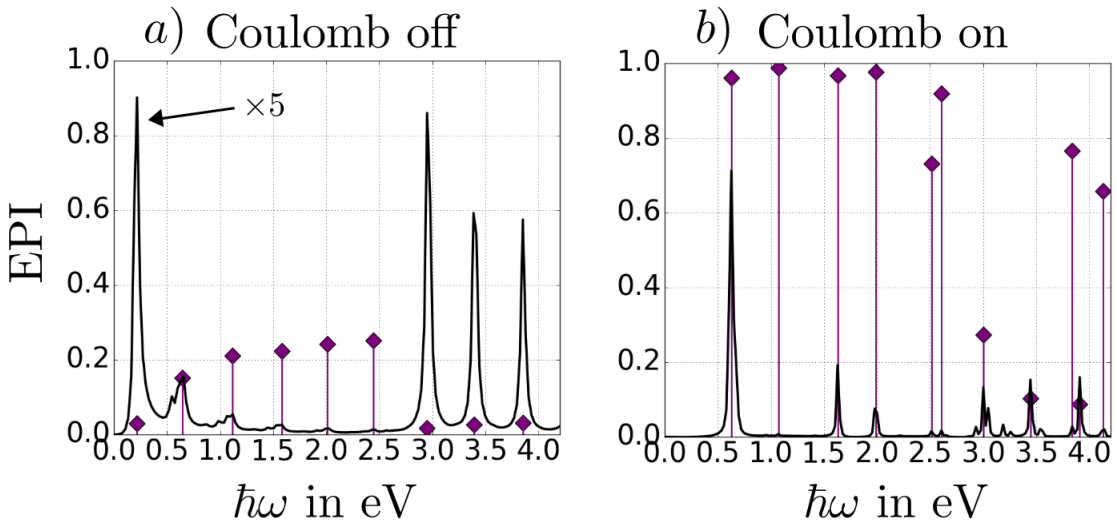

Figure S2: Comparison of the EPI (purple diamond elements) of the 8-fold doped dimer chain for Coulomb interaction turned off (a) and turned on (b). The latter case coincides with the data presented in the main body of the paper. The absorption cross section (black solid lines) of the noninteracting system has been scaled with a factor of 5 with respect to the absorption cross section of the interacting system.

EPI without Coulomb Interaction

Figure S2 shows a comparison of the absorption cross sections (black solid lines) and the energy-based plasmonicity indices (EPIs, purple diamond elements) of the 8-fold doped dimer chain. We can see that the resonances in the noninteracting system (a) have EPIs well below 0.3 and are classified single-particle-like. On the contrary, in the interacting system (b), plasmons can form as a consequence of the electron-electron interaction. We notice here, that the EPI systematically faces difficulties in properly characterizing intra-band single-particle-like transitions, like the ones in the noninteracting system below 2.5 eV. This is due to the energy mesh provided by the TB simulation method and can be circumvented by investigating larger structures or employing more sophisticated simulation methods that allow for finer energy resolution (more single-particle energy states per atom in the structure). On the other hand, the inter-band single-particle-like transitions above 2.5 eV have an EPI below 0.05.

Relation of the EPI and the Scaling Approach

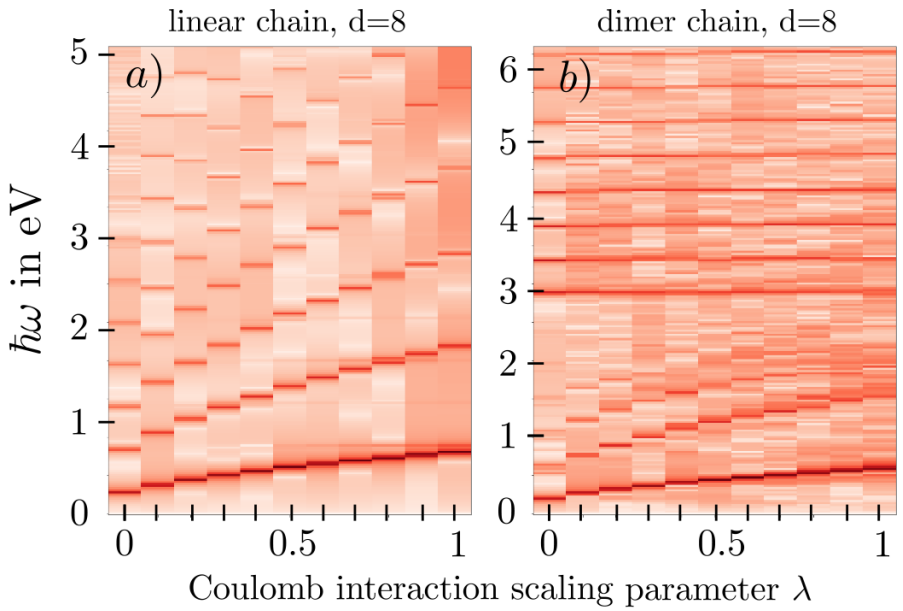

Figure S3: Absorption cross sections of the 8-fold linear (a) and dimer (b) chains as a function of the Coulomb interaction scaling parameter λ. The noninteracting system is represented by $\lambda = 0$, whereas $\lambda = 1$ corresponds to the Coulomb interaction fully taken into account with Coulomb matrix values as reported in the main body of the paper.

Figure S3 shows the absorption cross sections of the 8-fold linear (a) and dimer (b) chains as a function of the Coulomb interaction scaling parameter λ, which enters the induced potential of Eq. 4 of the main body of the paper,

$$\varphi_l^{\mathrm{ind}}(t) = -\lambda e N_e \sum_{l'} v_{ll'} \left(\rho_{l'l'}(t) - \frac{1}{N} \right).$$

From the qualitative discussion of the linear chain, we presumed all the prominent resonances of the spectrum to be plasmonic. In the scaling approach, they should undergo a spectral shift when the interaction energy is modified, in accordance with Fig. S3a. On the other hand, the 8-fold doped dimer chain supports both single-particle-like and plasmonic resonances. In the absorption cross section in Fig. S3, we can see that the prominent resonances well below 3 eV blue-shift with increasing electron-electron interaction. It originates from Fig. S2b that the EPI classifies these resonances as plasmonic. On the other hand, the prominent

resonances close to 3.0 eV, 3.4 eV, and 3.9 eV remain spectrally stable for different interaction strengths. The EPI of these three resonances has values below 0.3 and are therefore classified predominantly single-particle-like. This is in accordance with the scaling approach.

EPI of the 20-fold Doped Dimer Chain

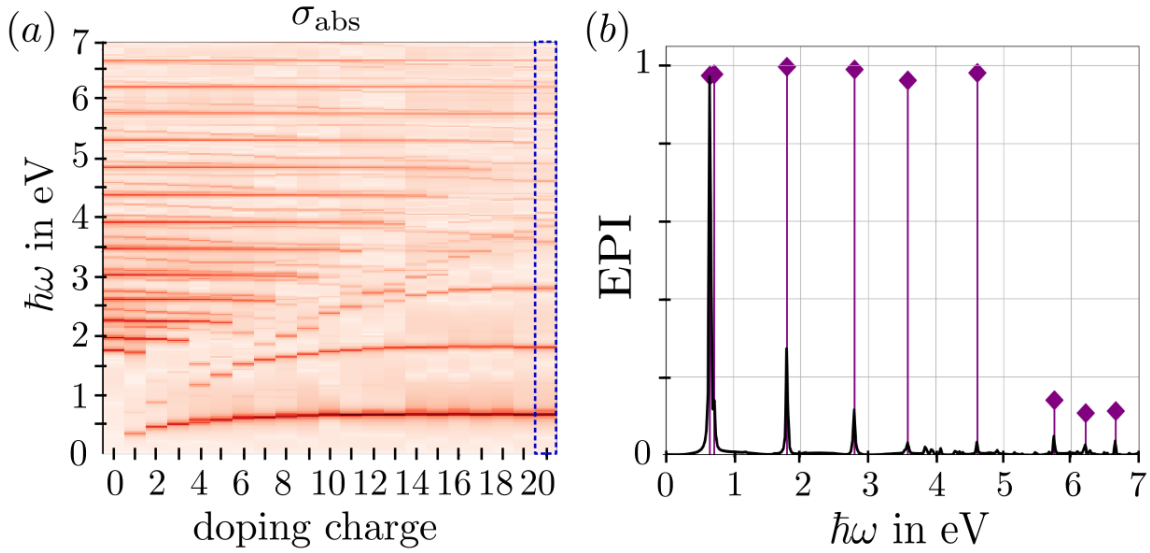

Figure S4: (a) Absorption cross section of the dimer chain with $N = 70$ atoms for various doping levels. (b) EPI (purple diamond elements) and absorption cross section (black solid line) of the 20-fold doped chain with $N = 70$ atoms.

Figure S4a, for convenience, again shows the absorption cross section of the dimer chain for various doping levels (see Fig. 3b of the main body of the paper). Fig. S4b presents the EPI (purple diamonds) of the 20-fold doped dimer chain with $N = 70$ atoms alongside with its absorption spectrum (black solid line). All resonances below 5 eV exhibit an EPI close to unity, which renders them plasmonic. In particular, this applies as well for the second (third) plasmonic mode at 1.8 eV (2.8 eV), which lies close to (well above) the HOMO-LUMO energy gap of 1.67 eV. Moreover, it is in agreement with the interpretation of Fig. S4a, where we observe spectral shifts for all these resonances as a function of the doping charge. Conversely, the three resonances above 5 eV exhibit an EPI well below 0.2 and are classified single-particle-like. In Fig. S4a, we observe that they are already present in the

undoped structure and spectrally stable if the doping charge is varied. We therefore conclude that the EPI can reliably distinguish plasmonic from single-particle-like resonances not only inside the HOMO-LUMO gap, but also for modes that are located close to and above the gap.

EPI of Polyacene Chains

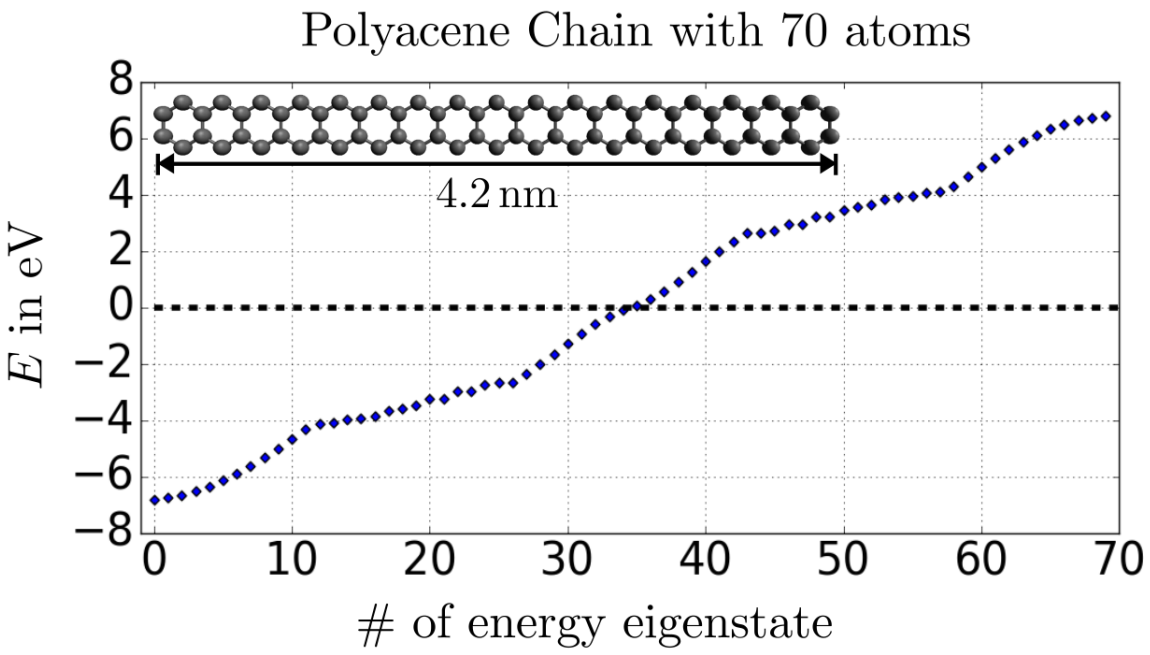

Figure S5: Energy landscape of the zigzag-edged polyacene chain with $N = 70$ atoms (shown in the inset). The dashed horizontal line corresponds to the particle-hole symmetry line and coincides with the Fermi energy in the undoped structure.

Figure S5 shows the energy landscape of the zigzag-edged polyacene chain with $N = 70$ atoms and a real space illustration in the inset. Figure S6 shows its absorption cross section as well as the EPI for d=0 and $d = 4$ doping electrons. The chain has zigzag edges on its long side. Although the absorption cross section shows a similar behavior as the one of the dimer chain, the polyacene chain behaves energetically different. Its energy landscape does not exhibit a bandgap. However, the HOMO state has a vanishing transition dipole matrix element with the 9 next states of higher energy (LUMO until LUMO+8), which effectively

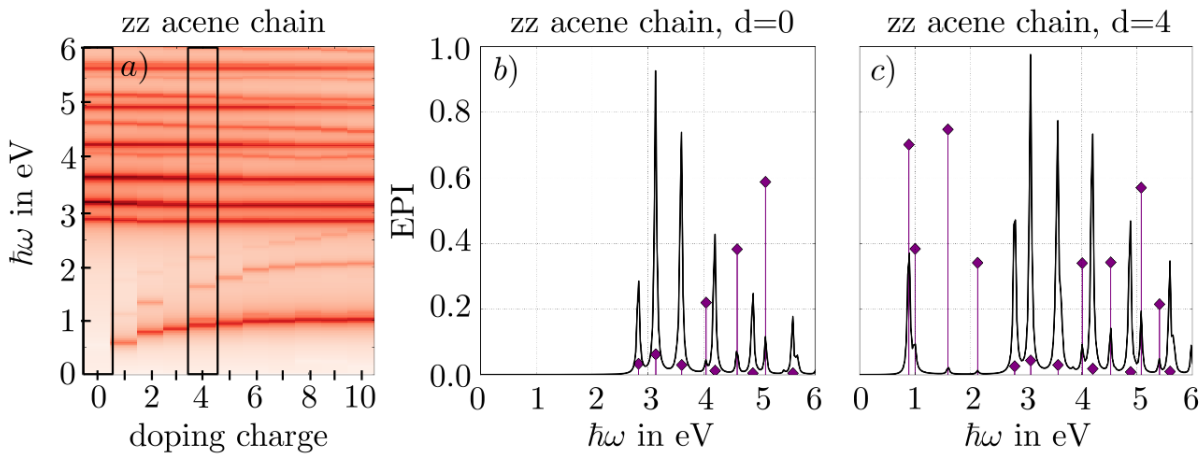

Figure S6: (a) Absorption cross section for a zigzag-edged polyacene chain with $N = 70$ atoms as a function of doping charge. (b) EPI (purple diamond elements) and absorption cross section (black solid line) for the neutral system. (c) EPI (purple diamond elements) and absorption cross section (black solid line) for the 4-fold doped system.

opens a transparency window in the low-energy region for dipolar plane wave excitation. In the undoped structure, all prominent resonances are classified single-particle-like. However, we also find three peaks of comparably small relative height, emerging around 4 eV, 4.5 eV, and 5.1 eV, with considerably higher EPI. In Fig. S6a, one can see that these smaller hybrid resonances are weakly dispersive (which is generally a plasmonic feature), whereas the other single-particle-like prominent resonances are spectrally stable. Upon doping, the most evident modification of the absorption cross section is the emergence of low-energy resonances with comparably high EPI (see Fig. S6c), qualitatively equivalent to the 8-fold doped dimer chain example of the main body of the paper.