SUPPORTING INFORMATION FOR: Light-induced field enhancement in nanoscale systems from first-principles: the case of polyacenes

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S1: Ground state electronic properties of acenes

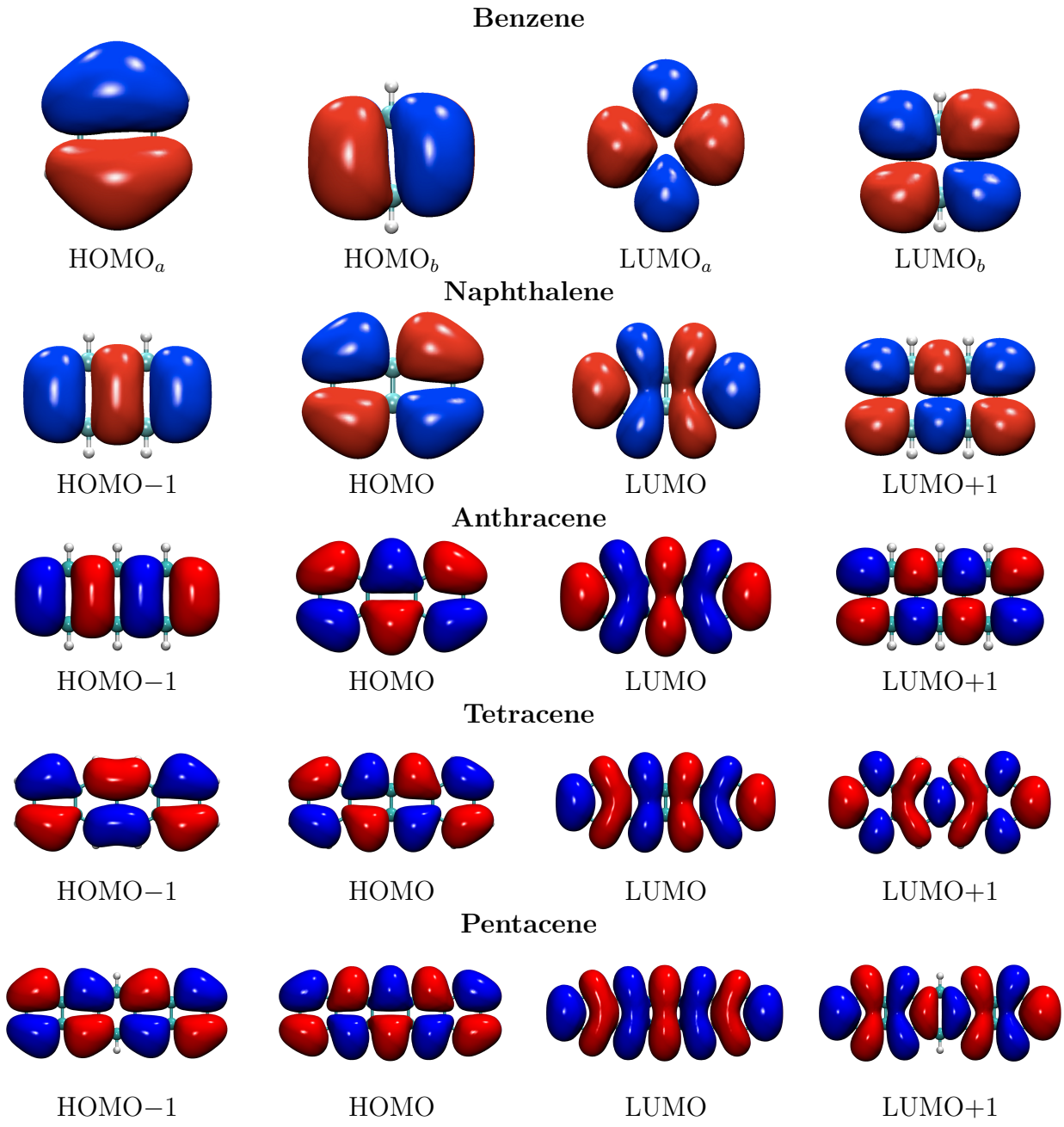
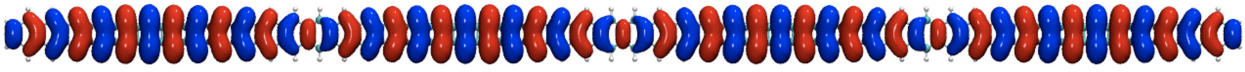
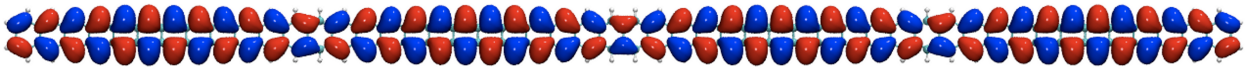


Figure S1: *Isosurface plots of selected frontier orbitals for benzene, naphthalene, anthracene, tetracene and pentacene. Blue and red colors refer to positive and negative values of the orbital wavefunction, respectively. The state is indicated under each figure. Since benzene has double degenerate HOMO and LUMO states, they are labelled with a subscript (a or b).*

50-acene



HOMO−1



LUMO+1

Figure S2: *Isosurface plots of KS HOMO−1 and HOMO+1 molecular orbitals for the 50-acene. Blue and red colors refer to positive and negative values of the orbital wavefunction, respectively.*

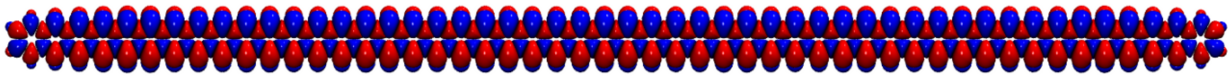


Figure S3: *Isosurface plots of the spin polarization (difference between spin up and spin down charge density) of the 50-acene. Blue and red colors refer to positive and negative values of the spin polarization, respectively.*

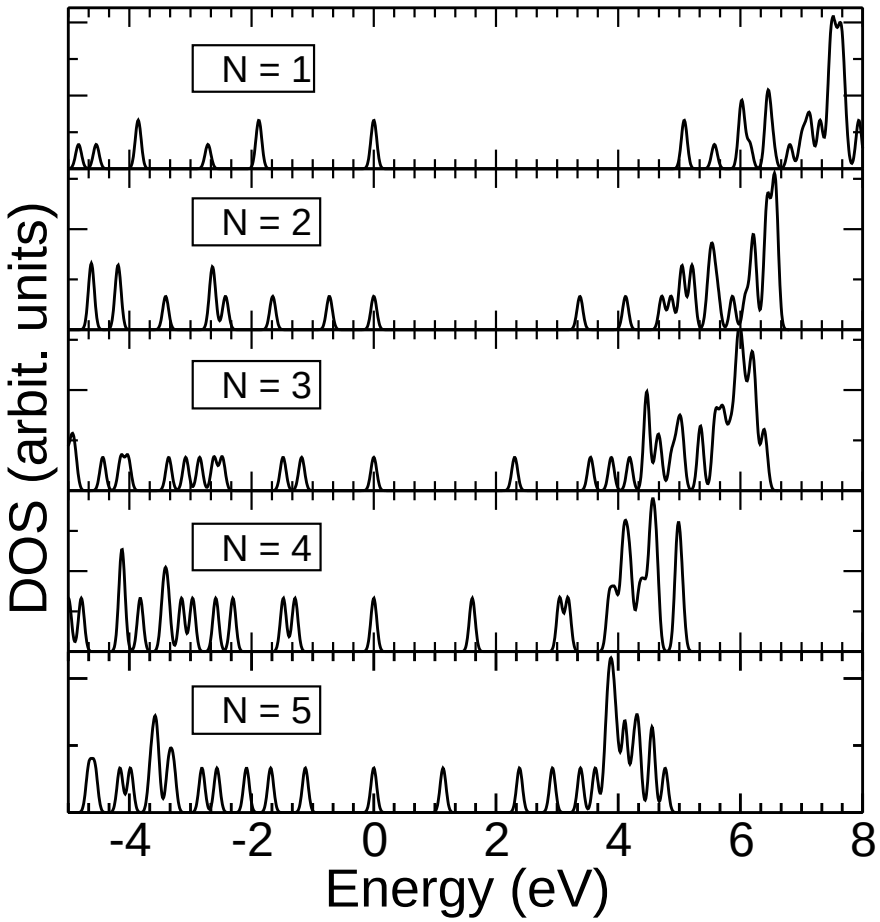


Figure S4: *DOS of benzene, naphthalene, anthracene, tetracene and pentacene, where the HOMO energy is set to zero.*

S2: Convergence of the spectra w.r.t. the energy cutoff

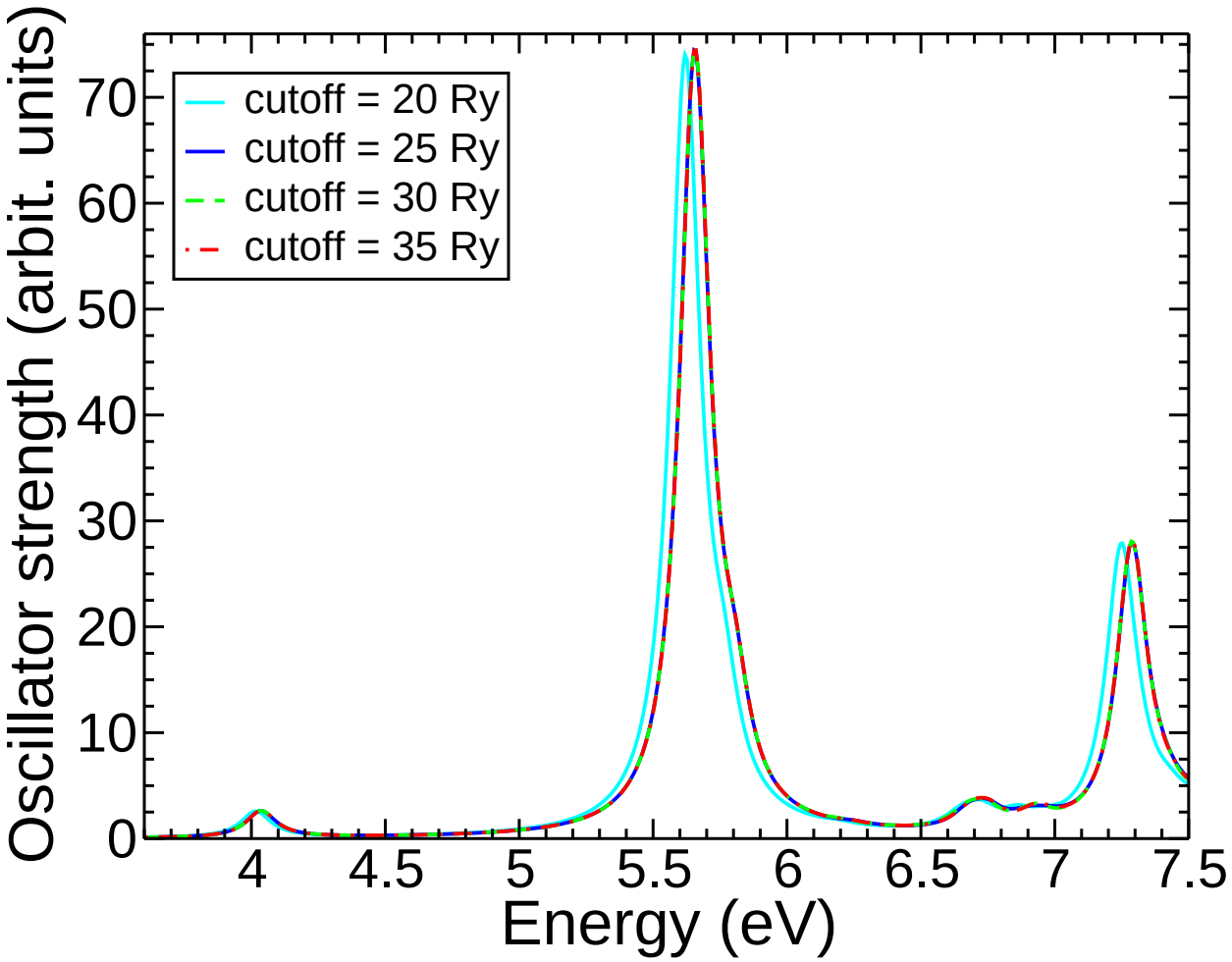


Figure S5: *Low energy absorption spectra of naphthalene: comparison between PBE calculations with different energy cutoffs for the expansion of wavefunctions in plane waves basis set.*

S3: PBE vs B3LYP

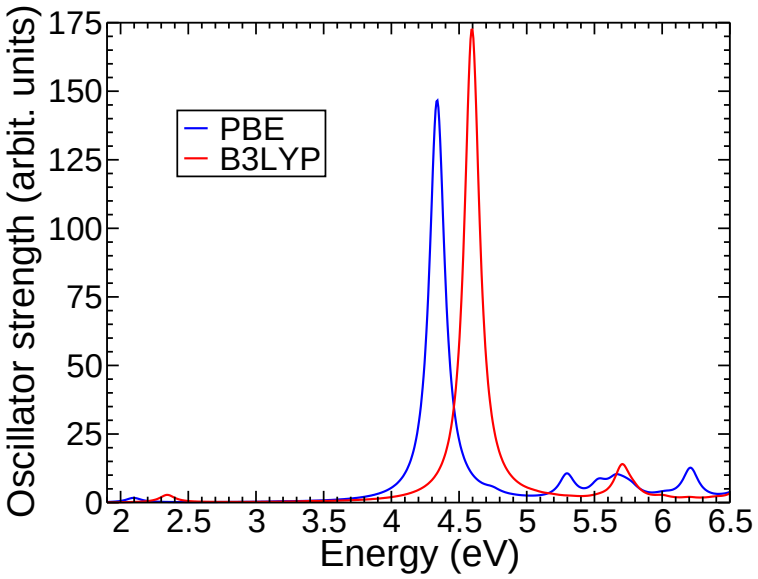


Figure S6: *Low energy absorption spectra of tetracene: comparison between PBE and B3LYP calculations.*

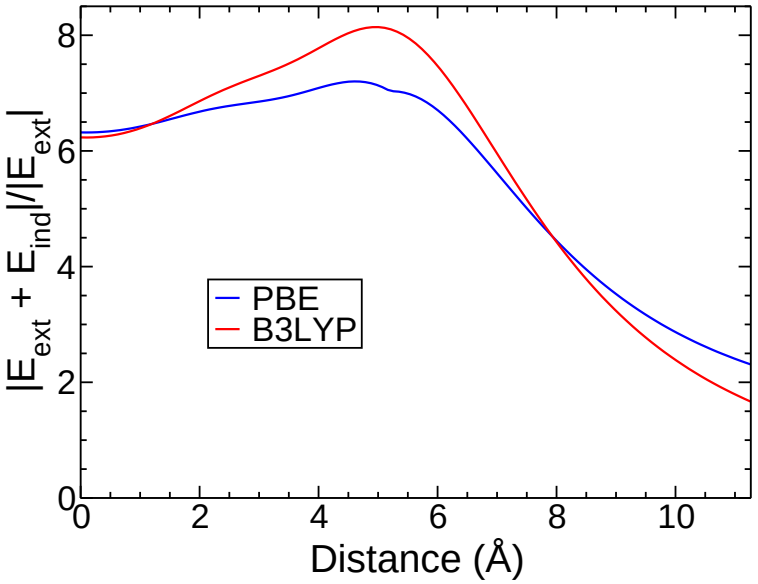


Figure S7: *Electric field enhancement of longitudinally polarized excitations of the tetracene, computed along the axis of the molecule, 3.3 Å above its plane: comparison between PBE and B3LYP calculations. The distance indicated in the x axis refer to the distance from the center of the molecule, on the considered plane.*

S4: Response charges and electron-hole analysis of optical transitions

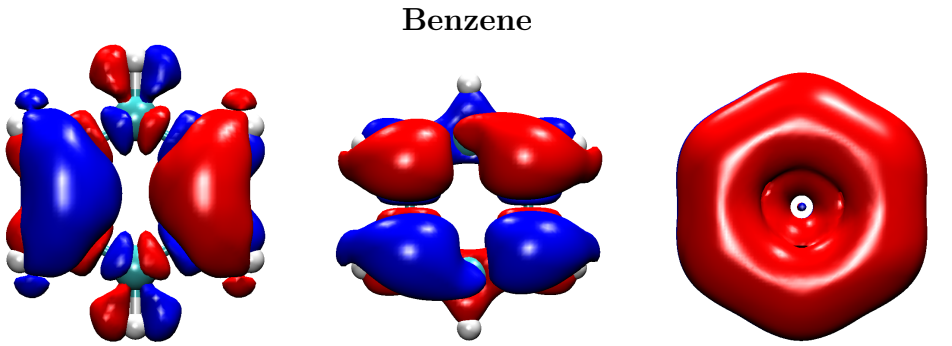


Figure S8: *Isosurface plots of the imaginary part of the response charge density of benzene. The polarization of the incoming field and the peak at whose frequency the response is calculated are also indicated. Blue and red colors refer to positive and negative values of the response charge density, respectively.*

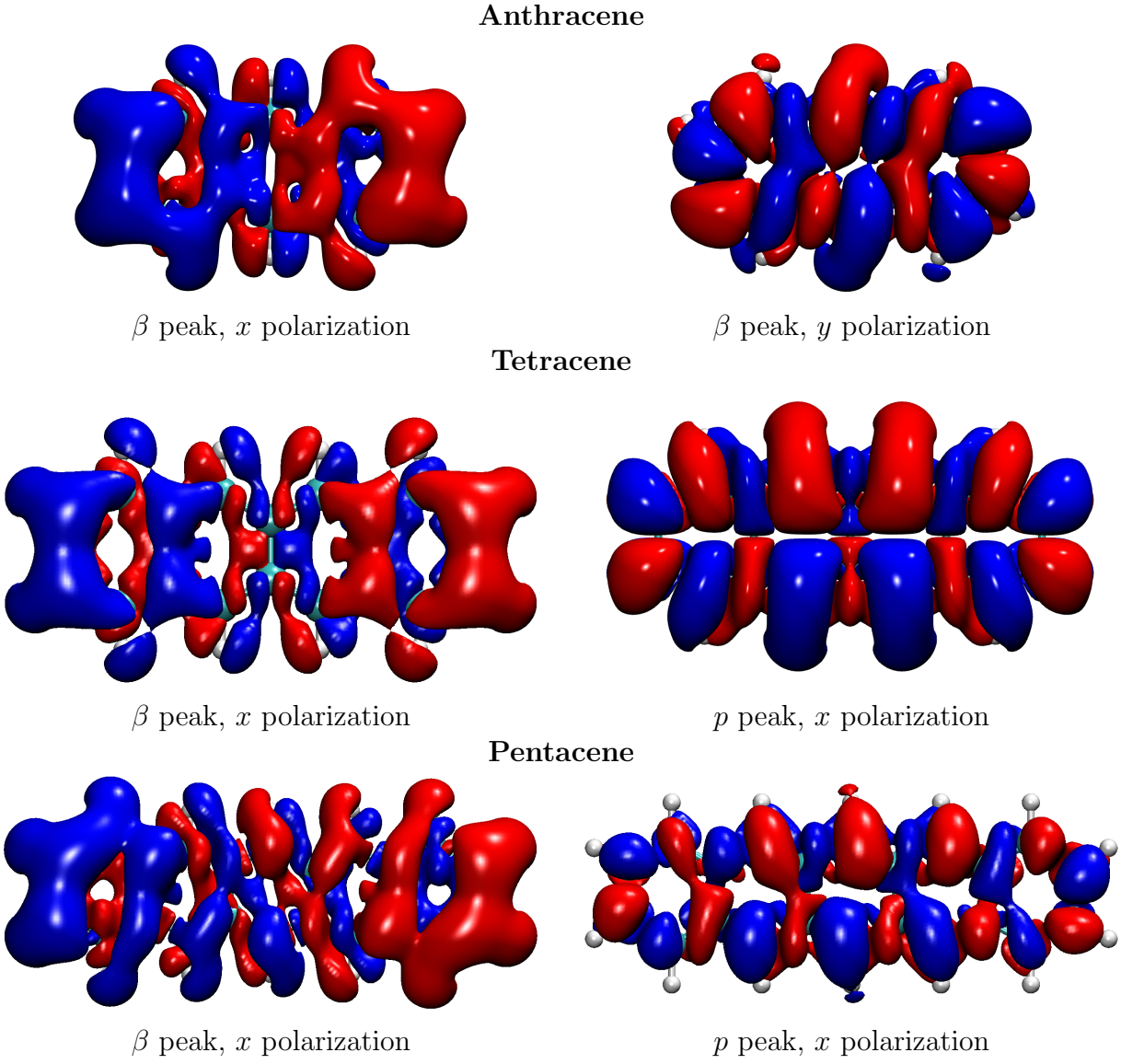


Figure S9: *Isosurface plots of the imaginary part of the response charge density of anthracene, tetracene and pentacene. The polarization of the incoming field and the peak at whose frequency the response is calculated are also indicated. Blue and red colors refer to positive and negative values of the response charge density, respectively.*

Table S1: *Main electron-hole components ξ_{vc} of the lowest-energy peaks of benzene, normalized such that $\sum_{vc} \Im\left(\xi_{vc}\right)^2 = 1$ and expressed in percentage form.*

Benzene		
β peak, x polarization	β peak, y polarization	p peak, z polarization
HOMO_b LUMO_a 88%	HOMO_b LUMO_b 96%	HOMO_a LUMO+2 50%
HOMO_a LUMO_b 9.9%	HOMO_a LUMO_a 1.6%	HOMO_b LUMO+3 49%
HOMO_b LUMO+12 0.24%	HOMO_a LUMO+12 0.87%	HOMO_b LUMO+2 0.24%
HOMO_b LUMO+29 0.22%	HOMO_a LUMO+21 0.20%	HOMO_a LUMO+3 0.20%
HOMO_a LUMO_a 0.20%	HOMO−1 LUMO+3 0.15%	HOMO_a LUMO+13 0.038%

Table S2: *Main electron-hole components ξ_{vc} of the lowest-energy peaks of anthracene, normalized such that $\sum_{vc} \Im\left(\xi_{vc}\right)^2 = 1$ and expressed in percentage form.*

Anthracene	
β peak, x polarization	p peak, y polarization
HOMO−1 LUMO 50%	HOMO LUMO 37%
HOMO LUMO+1 44%	HOMO LUMO+1 34%
HOMO−4 LUMO+2 1.1%	HOMO−1 LUMO 19%
HOMO LUMO+5 0.98%	HOMO−2 LUMO+2 4.1%
HOMO LUMO+19 0.89%	HOMO−1 LUMO+1 3.7%

Table S3: *Main electron-hole components ξ_{vc} of the lowest-energy peaks of tetracene, normalized such that $\sum_{vc} \Im\left(\xi_{vc}\right)^2 = 1$ and expressed in percentage form.*

Tetracene	
β peak, x polarization	p peak, y polarization
HOMO LUMO+2 52%	HOMO LUMO 89%
HOMO−2 LUMO 41%	HOMO−1 LUMO+1 3.3%
HOMO−4 LUMO+1 2.1%	HOMO−2 LUMO+2 1.8%
HOMO−1 LUMO+11 1.8%	HOMO−3 LUMO+4 1.1%
HOMO−9 LUMO 0.52%	HOMO−5 LUMO+7 0.99%

Table S4: *Main electron-hole components ξ_{vc} of the lowest-energy peaks of pentacene, normalized such that $\sum_{vc} \Im\left(\xi_{vc}\right)^2 = 1$ and expressed in percentage form.*

Pentacene	
β peak, x polarization	p peak, y polarization
HOMO−2 LUMO 39%	HOMO LUMO 63%
HOMO LUMO+2 38%	HOMO−2 LUMO 12%
HOMO LUMO+3 14%	HOMO LUMO+2 11%
HOMO LUMO 1.9%	HOMO−1 LUMO+1 6.3%
HOMO−4 LUMO+1 1.3%	HOMO−2 LUMO+2 3.3%

S5: Electric field enhancement for single acenes

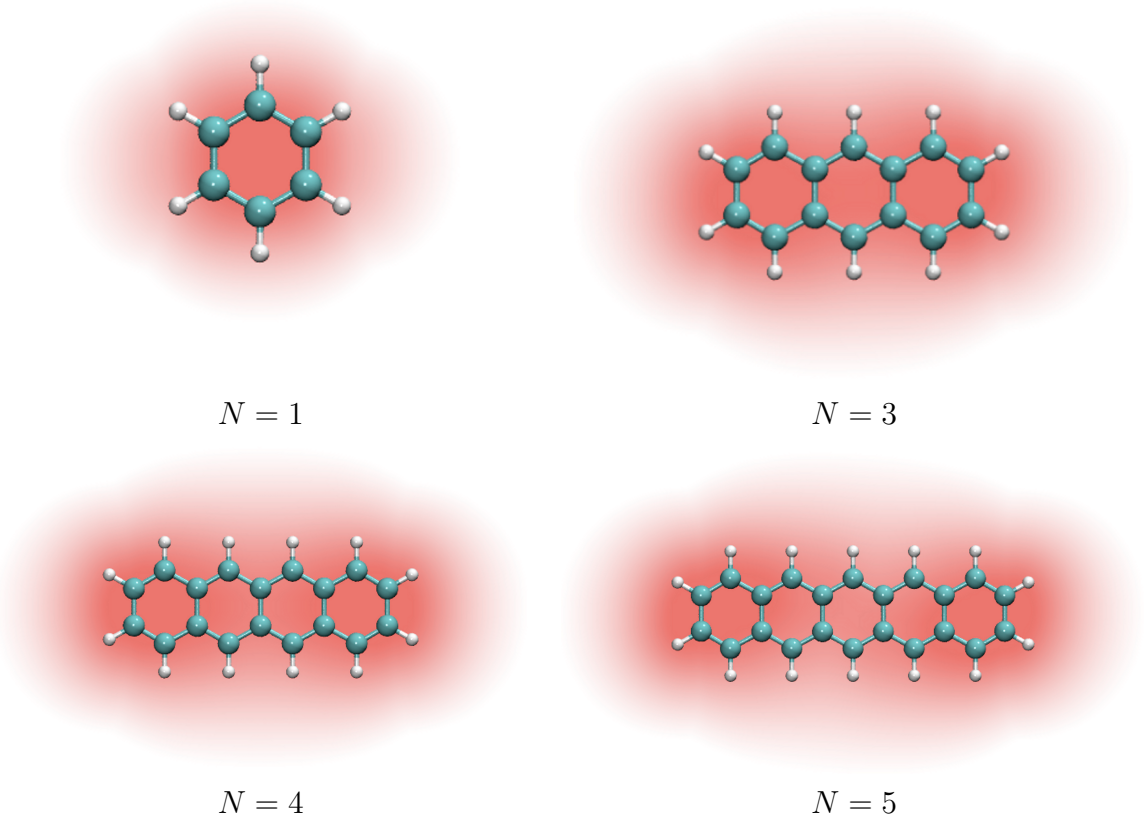


Figure S10: *Top view of 2D intensity plot representation of the induced electric field in the* (x, y) *plane, calculated* 3.3 *Å above the plane of the molecule. The numbers* N *of rings of the considered acenes are indicated.*

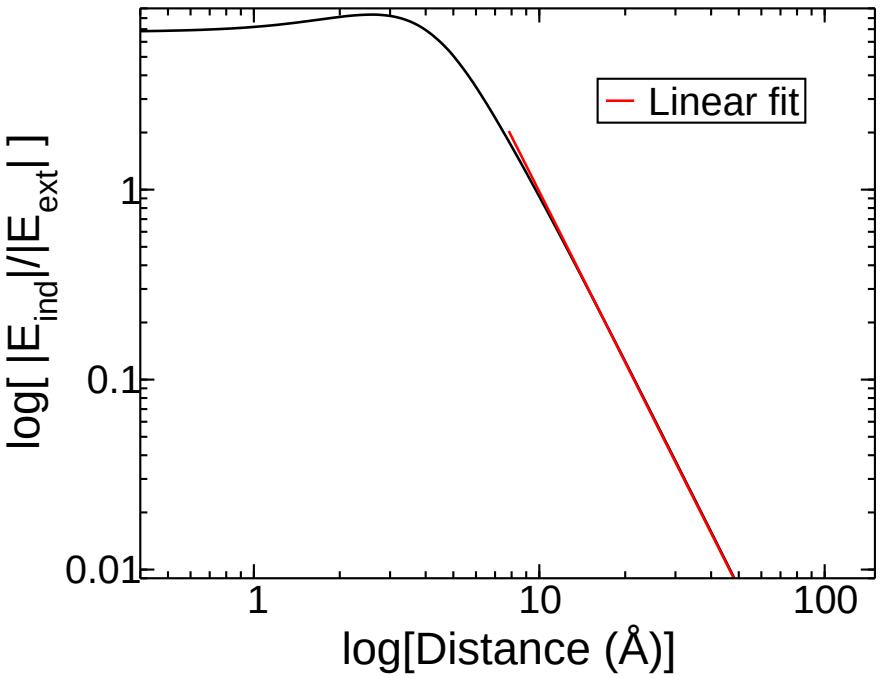


Figure S11: *Log-log plot of the calculated (black line) electric field decay as a function of the distance from the center of the molecule (naphthalene). Red line represents the analytical dipolar behavior* $E_{ind} \propto x^{-3}$.

S6: Optical absorption and electric field enhancement for naphthalene dimer

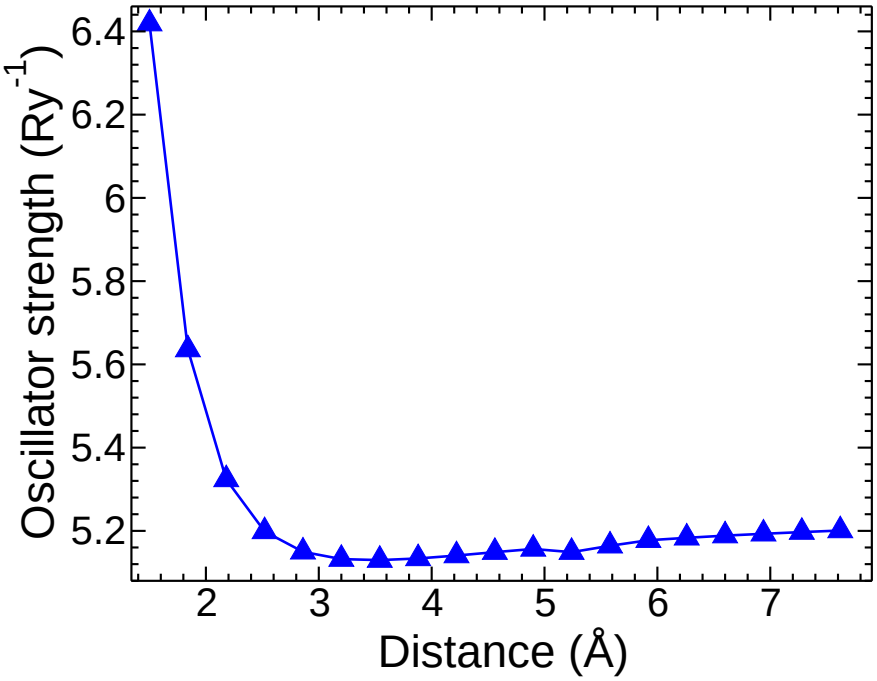


Figure S12: *Intensity of the low-energy absorption peak p of the dimer as a function of the distance d.*

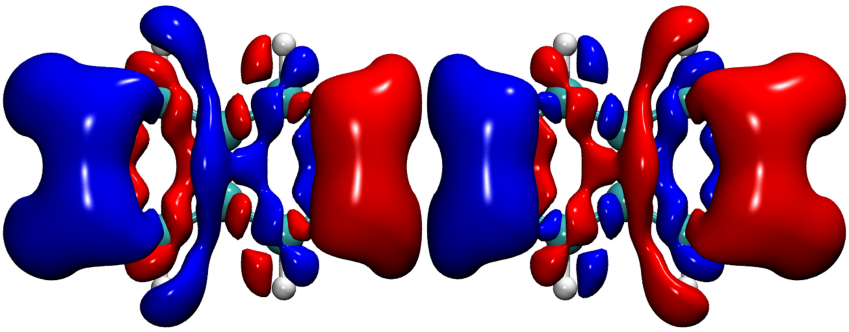


Figure S13: *Isofurface plot of the response charge density of naphthalene dimer, which can be modeled as two finite-size dipoles oscillating in phase.*

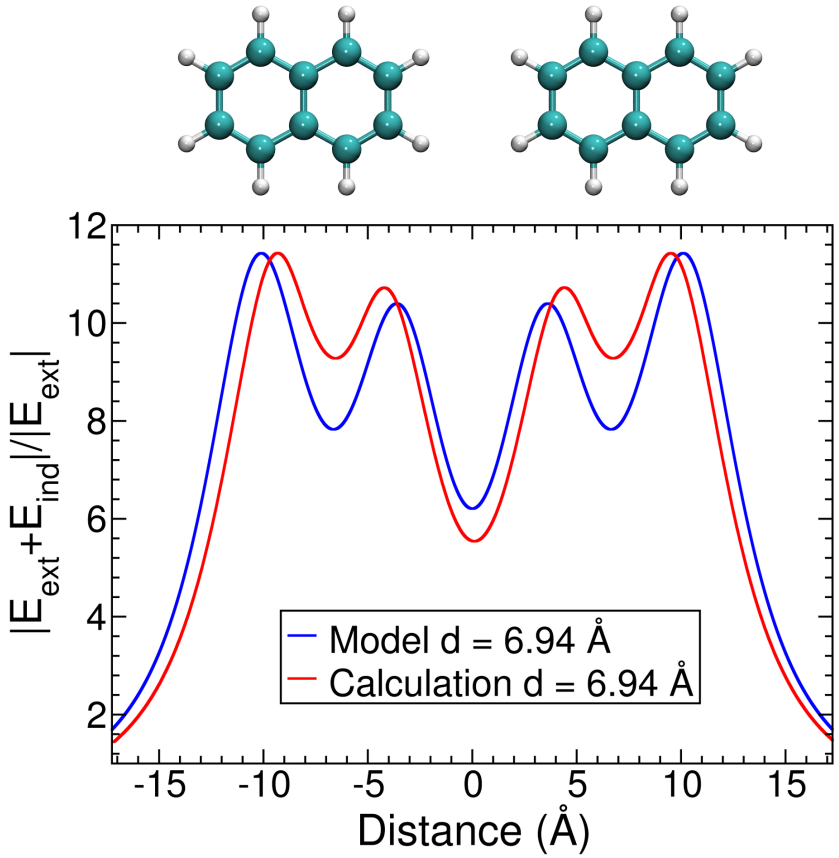


Figure S14: Electric field enhancement resulting from calculated response charge density (red line) and classical finite-size dipole model (blue). Dimer atomic structure is superimposed for clarity.