Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information for

Ultrafast, Asymmetric Charge Transfer and Slow Charge Recombination in Porphyrin/CNT Composites Demonstrated by Time-Domain Atomistic Simulation

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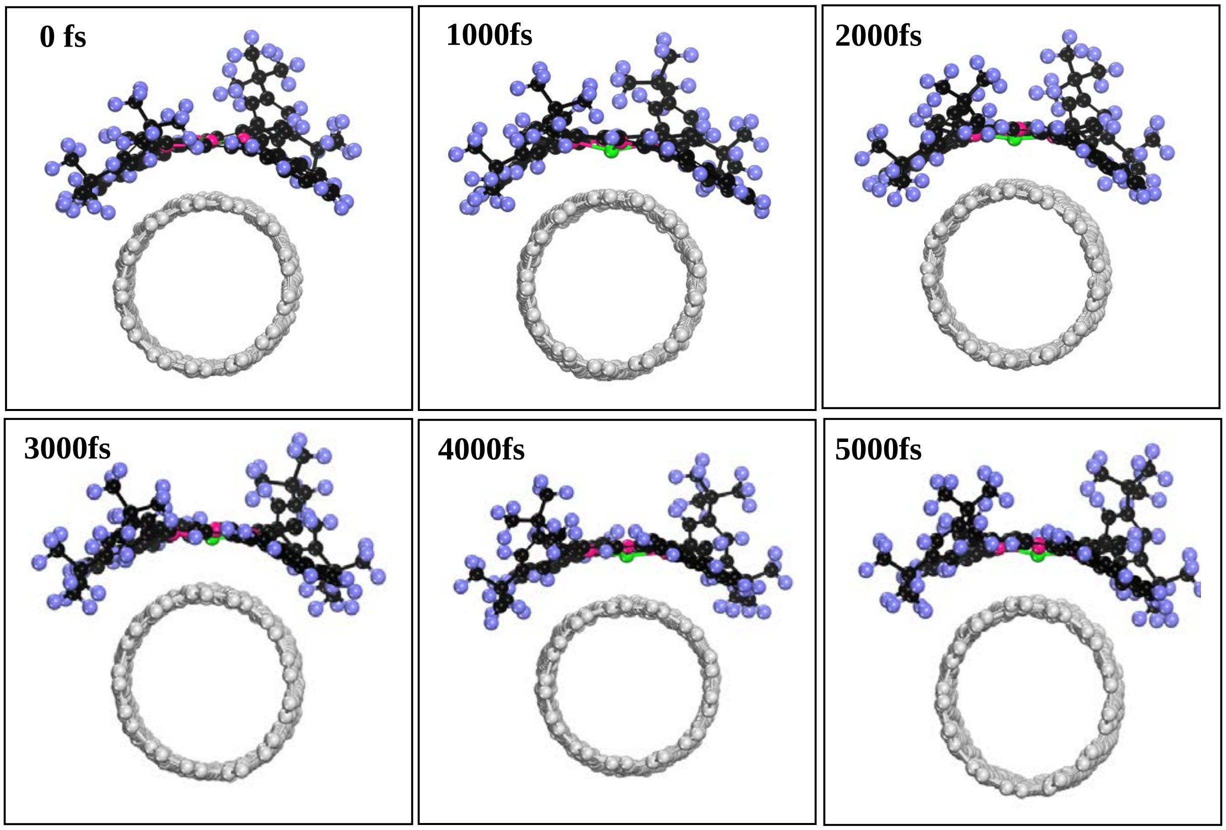

Figure S1. Structural evolution of the *anti*-porphyrin/CNT system along a molecular dynamics trajectory at 300 K.

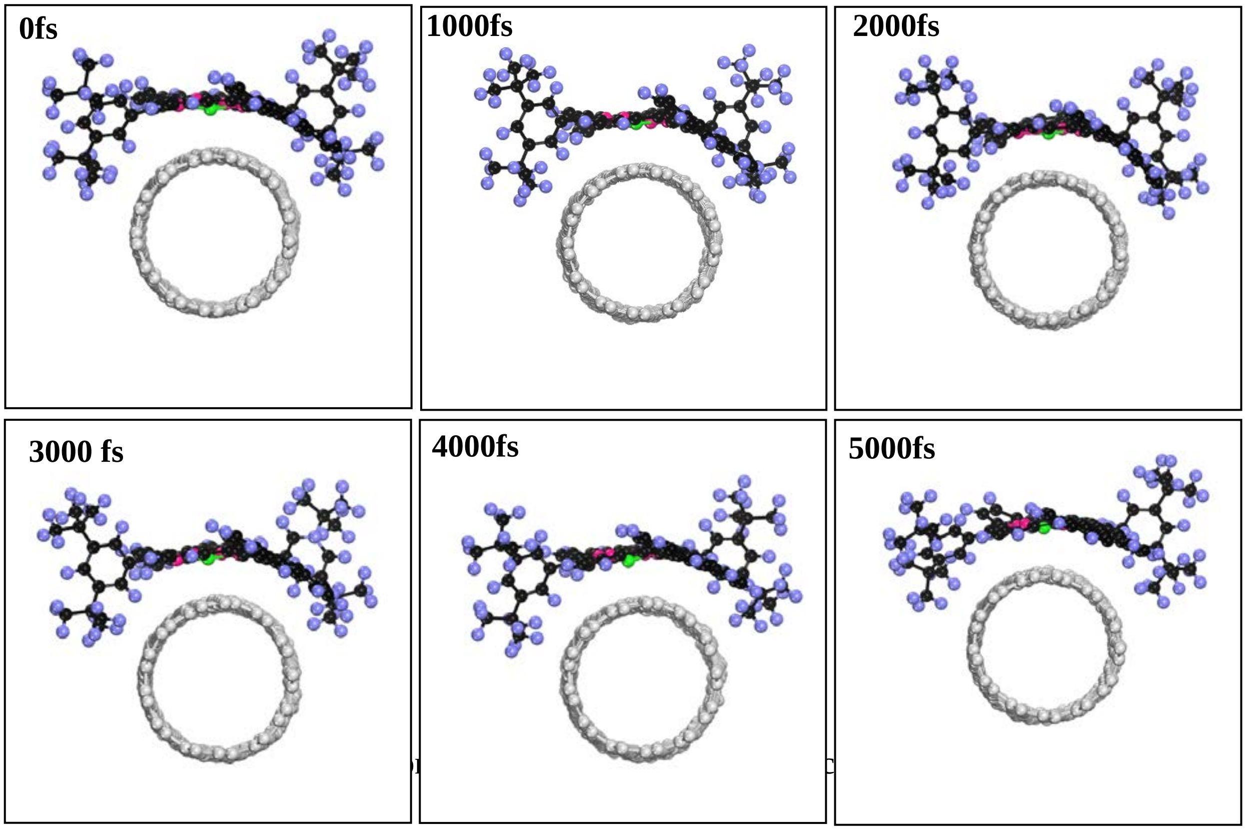

Figure S2. Structural evolution of the *syn*-porphyrin/CNT system along a molecular dynamics trajectory at 300 K.

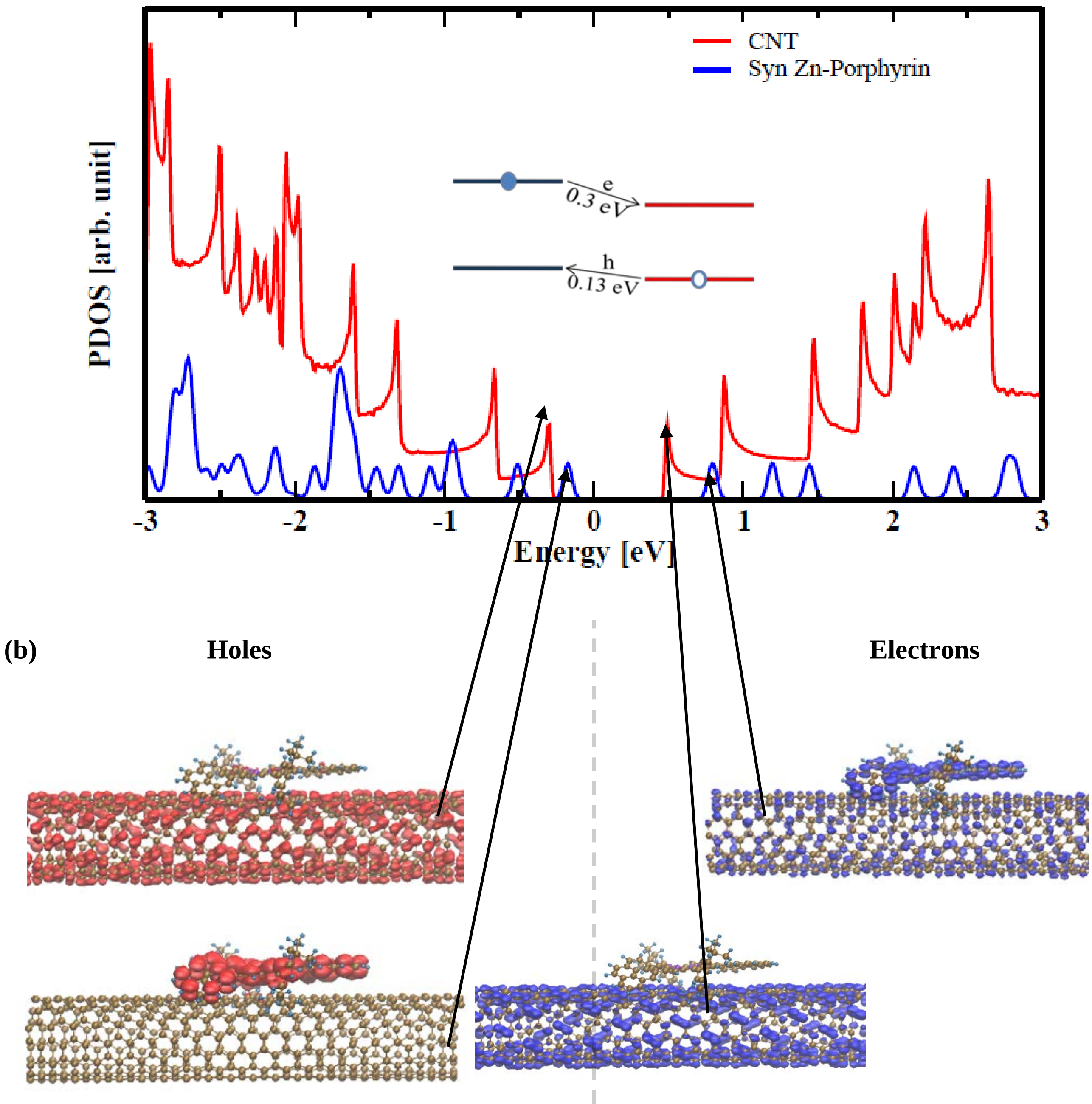

Figure S3. **(a)** Projected density of states (PDOS) of the *syn*-porphyrin/CNT system at 0 K.CNT has a much larger DOS than porphyrin. The CNT van Hove singularities and discrete energy levels of the porphyrin are maintained in the combined system, indicating that the porphyrin/CNT interaction is non-covalent. The insertshows the energy offsets providing the driving force for the electron and hole transfer.**(b)**Charge densities of the donor and acceptor states for the hole and electron transfer.The vertical arrows between panels (a) and (b) relate the donor and acceptor orbital densities to the orbital energies. The electron donor state is delocalized between porphyrin and CNT, while the hole donor state is strongly localized onCNT. Both acceptor states are localized on the corresponding systems. Compare to Figure 3 of the main text showing the same data for the *anti*-porphyrin/CNT system.

Calculation of Pure-Dephasing Times

The pure-dephasing time is associated with fluctuations of energy levels due to the coupling of electrons to phonons. The fluctuations of the energy levels are well characterized by correlation functions. The un-normalized autocorrelation function (ACF) for a transition of energy gap$E$ is defined as

$$C_u(t) = \left\langle \Delta E(t) \Delta E(0) \right\rangle, \tag{S1}$$

where $\Delta E=E-<E>$ is the deviation of the instantaneous energy gap from the statistically averaged value $<E>$, in present in the canonical ensemble.Note that $E$is the transition energy and not the energy of a particular level. The initial value of the un-normalized ACF gives the average fluctuation in the transition energy, $C_u(0)=<E^2(0)>$. Dividing $C_u(t)$ by $C_u(0)$ gives the normalized ACF:

$$C(t) = \frac{\left\langle \Delta E(t) \Delta E(0) \right\rangle}{\left\langle \Delta E^2(0) \right\rangle} \; . \tag{S2}$$

ACFs characterize periodicity and the memory of the energy gap fluctuation. A rapid decay of ACF implies fast loss of phase information, i.e. dephasing, and occurs if multiple phonon modes couple to the electronic transition.

Fourier transform of the ACF produces spectral density, also known as influence spectrum,

$$I(\omega) = \left| \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dt\, e^{-i\omega t} C(t) \right|^2 , \qquad \text{(S3)}$$

which identifies the phonon modes that couple to the electronic transition and are involved in the dephasing process. The peaks of the spectra indicate the strength of the electron-phonon coupling for the phonon modes of given frequencies. The presence of multiple frequencies in the spectral density usually leads to a rapid ACF decay.

The optical response function considered below characterizes the pure-dephasing process for a pair of states entangled in a coherent superposition. The pure-dephasingfunction is computed using the second-order cumulant expansion to the optical response function,[1]

$$D_{cumu}(t) = \exp(-g(\mathrm{t})) , \qquad \text{(S4)}$$

where $g(t)$ is computed by double-integration of the unnormalized ACF,

$$g(\mathrm{t}) = \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 C_u(\tau_2) . \qquad \text{(S5)}$$

The pure-dephasing function decays fast if $C_u(t)$ decays fast and/or if the energy gap fluctuation, given by $C_u(0)$, is large.[2] The decoherence timescales were obtained by fitting the pure-dephasing functions, Eq. (S4), to a Gaussian.

References:

1. S. Mukamel, *Principles of nonlinear optical spectroscopy*, Oxford University Press on Demand, **1999**.
2. A. V. Akimov and O. V. Prezhdo, *J. Phys. Chem. Lett.*, 2013, **4**, 3857-3864.