ABSTRACT: Understanding energy transfer is of vital importance in a diverse range of applications from biological systems to photovoltaics. The ability to tune excitonic coupling in any of these systems, however, is generally limited. In this work, we have simulated a new class of single-molecule spectroscopy in which force microscopy is used to control the excitonic coupling between chromophores. Here we demonstrate that the excitonic coupling can be controlled by mechanical manipulation of the molecule (perylenediimide dimers and terylenediimide-perylenediimide heterodimers) and can be tuned over a broad range of values (0.02–0.15 eV) that correspond to different regimes of exciton dynamics going from the folded to the elongated structure of the dimer. In all of the systems considered here, the switching from high to low coupling takes place simultaneously with the mechanical deformation detected by a strong increase and subsequent decay of the force. These simulations suggest that single-molecule force spectroscopy can be used to understand and eventually aid the design of excitonic devices.
techniques. This new SMFS opens the possibility to investigate excitonic physics at an unprecedented level of detail and to design new excitonic devices where the exciton dynamics is controlled externally.

Realistic Model System. To test the potential of this SMFS, we consider systems consisting of two chromophores connected by a bridge where an external force is used to control the separation between the chromophores. Specifically, we investigate two classes of molecules: one formed by two perylenediimide units (PDI) and the other formed by one PDI and one terylenediimide (TDI). The two chromophore units are connected through an aliphatic chain, the bridge, with \( n \) CH\(_2\) groups (where \( n = 2−5 \)), and the extremities are each linked to an oxylipidic chain, the linkers (see Figure 1b). These chromophores are suitable candidates for this experiment because of their optical stability, large extinction coefficients, and high fluorescence quantum yields. The overlap of the PDI emission and TDI absorption spectra makes this pair suitable for electronic energy transfer experiments.

The simulation of the pulling experiment is based on a constrained Molecular Dynamics (MD) scheme with details similar to those used in refs 38−41 and provided in the Supporting Information (SI). Briefly, the elongation is obtained by the application of a stiff isotropic potential on one terminal carbon atom that mimics the attachment to a surface, while the other terminal carbon is connected to a virtual harmonic spring, simulating the AFM cantilever. The excitonic coupling presented in the main Letter is computed using the transition atomic charge method\(^{12}\) and therefore includes only the Coulombic contribution and will be indicated as \( J_C \). To calculate the excitonic coupling, the PEG linkers and all of the atoms of the bridge were removed from the conformations of the MD trajectory. The atomic transition charges were computed once using TD-DFT/LRC-ωPBEh/6-31G\(^*\)\(^{43}\) from an isolated chromophore unit (PDI or TDI respectively), following the definition in eq S1 ref. 42 (a full definition is also reported in the SI).\(^{44}\) As shown in the SI, we have verified that the contribution of short-range interaction\(^{45}\) is small and can be neglected for the system studied here, and thus, \( J_C \) provides a good estimate of the total exciton coupling.

**Figure and Excitonic Coupling Spectroscopy.** The results from the simulation of the force (\( F \))−exciton coupling spectroscopy for molecules PP2 and PP3 as a function of the end-to-end molecular length \( \xi \) are shown in Figure 2. The predominant conformations along the pulling experiment of both PP2 and PP3 are shown in Figure 3 (see also Figures S4−S6 in the SI for a more complete set of images). Consider first the \( F \)−exciton spectroscopy of PP2 (Figure 2a). At \( \xi < 6 \) Å, the molecule is compressed, which leads to a negative force. Upon elongation, the force depends weakly on the displacement (6 Å < \( \xi \) < 15 Å). In this region, the PP2 conformations essentially form a quasi-\( \pi \)-stacked structure at \( \xi = 5 \) Å followed by a fully \( \pi \)-stacked structure at \( \xi = 12 \) Å (Figure 3 top panel). At around \( \xi = 20 \) Å, a force peak is observed: the increase in the force followed by its drop denotes a mechanical transition from a mechanically stable structure to another one. Before the transition, the molecule forms a stable conformation (\( \xi = 17 \) Å, Figure 3 top panel) as both the potential energy \( U \) and the potential of mean force (PMF) \( \phi \) (equivalent to the Helmholtz free energy) in Figure 2c show. At increased elongation, the applied force overcomes the \( \pi \)-stacking interactions and the molecule assumes a gauche conformation (\( \xi = 22 \) Å, Figure 3 top panel). Overcoming the \( \pi \)-stacking interactions causes an increase in both the free energy and potential energy.\(^{46}\) This conformational change significantly affects the excitonic coupling (Figure 2e). Between \( \xi = 5 \) and 20 Å, the average coupling oscillates at around 0.14 eV. At the transition point, it drastically drops to ~0.06 eV. Upon further elongation, another force peak signals a mechanical transition at around \( \xi = 32 \) Å: the weak \( \pi \)-stack interactions of the gauche conformation are stretched until the molecule is fully elongated (see conformations at \( \xi = 28 \) and 34 Å). This region is also characterized by a concave region of the PMF, which indicates a mechanically unstable region. Here, the intermediate coupling decreases until it reaches its minimum value as the PDI units are at the farthest possible distance.

Similarly, a force peak indicates the \( \pi \)-stacked conformation breaking point for PP3. At this elongation, the excitonic coupling decreases, but contrarily to PP2, we find no intermediate region between the high and low coupling plateaus. This result is consistent with the finding of a single force peak at \( \xi = 22 \) Å. Note the both larger breaking force and free energy difference of this system when compared to PP2 (Figure 2c,d). When the molecule is fully stretched, the low coupling plateau is now lower with respect to PP2 due to the longer bridge that allows the PDI units to lie at a longer distance. Another difference is the increased stability of the \( \pi \)-stacked conformation of PP3 with respect to PP2: the PP2 \( \pi \)-stacked conformation is destabilized by both the strained N−C−C angles of the bridge and the repulsive interactions between the oxygen atoms. The excellent correlation between the critical points in the force spectroscopy and those in the excitonic coupling map demonstrates that, by monitoring the...
force, one can control the magnitude of the excitonic coupling through mechanical deformation of the molecule.

Excitonic Coupling Change while Pulling. Figure 4 shows the average force and the histogram of the excitonic coupling for molecules PP2, PP3, PP4, and PP5 versus the end-to-end molecular distance $\xi$. For all homodimers, the strong coupling regimes are measured in a region where the $\pi$-stacking interactions are strong and the free energy shows a mechanically stable phase (SI Figure S2). This demonstrates that the geometries responsible for a large coupling are not artifacts that come from nonphysical structures. Note that the difference in free energy between 5 and 12 Å (the two stable conformers for short extensions) is smaller than the thermal energy for all molecules studied in this work (SI Figures S2 and S3). In all four cases, the major force peak is situated at the excitonic coupling switching region. The position of the peak is
constant as the bridge becomes longer: the breaking point is determined by the lengths of the PEG linkers (7.6 Å each and 3.6 Å for the π-stack distance; a total of ca. 19 Å). The coupling switch is abrupt, that is, from ~0.15 to ~0.03 eV over a few Angstroms.

The range of excitonic coupling explored in the pulling experiment is not much affected by the bridge length (the lowest coupling slightly decreases for longer bridges), but the latter affects the conformational space of the chromophores’ units. Specifically, for PP2 and PP4, we find a region of intermediate coupling magnitude (labeled by I in Figure 4ac), which is absent in either PP3 or PP5. The force shows that a second breaking event takes place at longer ξ only for even n, while when n is odd we find only a single peak in the force. The reason for this is found by the different angle between the principal axis of the PDI units (see transition dipole moments sketched in Figure 1 and the evolution of the angle between the transition dipole moments of the PDI units in Figure S7). When the π-stacked conformation is broken and n is 2 (even), the relative conformation of the CH2 groups of the bridge changes from staggered to gauche. The dihedral angle increases as the molecule is stretched; this is the conformation responsible for the intermediate coupling. For n = 3 (odd), the CH2 groups are already in gauche conformation with respect to each other; thus, stretching of the molecule causes the angle between the PDIs’ principal axes to increase (see transition dipole moments sketched in Figure 1), and the coupling decreases almost linearly until the CH2 groups are forced to assume an all-trans conformation that brings the PDIs further apart (see Figure S4). The cluster analysis of the trajectories shows that after the first peak an even number of CH2 molecules allows for long-range π interactions, while an odd number does not. This is due to the preferred all-trans conformation of an alkane chain and the respective angle with the PDI units.

Generally, we find that the longer the bridge, the longer the average distance between the center of mass of the PDI units, and thus, the magnitude of the coupling in the intermediate regime (labeled I in Figure 4) decreases from n = 2 to 4. For n = 4, it is already difficult to distinguish this region, and the even–odd effect described above becomes less important. Note also that the average force of the second peak for n = 4 is much lower than that for n = 2.

The force of the bridge affects the coupling transition: the shorter the bridge, the sharper the drop of the coupling. As the bridge length increases, the transition between the high and the low coupling regime becomes smoother; this is attributed to a larger number of degrees of freedom available when the bridge is long.

The effect of modulation on the excited state can be estimated as λ/4, where λ is the reorganization energy for the exciton transfer, which, for the PDI molecule, was evaluated computationally as 0.29 eV (see the SI), in fair agreement with the value that can be extracted from the absorption/fluorescence spectra (e.g., 0.21 eV using the data from refs 48 and 49, where the PDI is attached to a solubilizing group). When the excitonic coupling becomes comparable with the hopping barrier, there is a transition between the incoherent and coherent regimes and the exact quantum mechanical propagation becomes more complex. It is therefore remarkable that the range of excitonic coupling accessible through this experiment allows one to study the exciton dynamics close to the coherent regime (with minimal elongation and Jc ≈ 0.15 eV) and in the purely incoherent regime (at large elongation and Jc in the ~0.01–0.03 eV range). Moreover, as the position of the force peak coincides with the strong to weak coupling switch, monitoring the force, one can switch between coherent and incoherent regime via mechanical manipulation.

An additional difference between the high and low coupling configurations is the nature of the excited eigenstates (S1 and S2). To illustrate the spectroscopic differences at different elongations, we report simulated absorption spectra for the PP2 and PP5 systems in Figure 5 (see also Figure S8 and S9).

Figure 5. Simulated absorption spectra for PP2 and PP5 computed every 0.2 Å elongation using a Gaussian line shape with σ = 0.03 eV. The dashed vertical line shows the lowest singlet excitation for PDI, $E_{S1} = 2.79$ eV.
the folded H-aggregate, the S₁ absorption from the ground state would be almost forbidden and the S₂ would be intense and blue-shifted with respect to the isolated chromophore. In the elongated J-aggregate, the S₁ absorption becomes intense and red-shifted, and S₂ absorption becomes forbidden. Fluorescence measurements can also indicate whether the chromophores are in the folded or elongated configuration: in the first case, the fluorescence would be suppressed, while in the second, it would be enhanced. It should be noted that H- and J-character depend on the relative sign of J_C and the transition dipole moments (in our simulations, the sign of J_C is constant and the H- and J-character are given by the relative orientation of μ₁ and μ₂).

Force spectroscopy can be applied also to heterodimers, for example, TDI and PDI (see Figure 1b). In this case, there is an overlap between the emission spectrum of PDI and the absorption spectrum of the TDI that allows energy transfer from PDI to TDI following selective excitation of the PDI molecule. The rate of energy transfer is controlled by the excitonic coupling: thus, it is again possible to control the exciton dynamics through mechanical manipulation. An additional complication that will not be addressed in detail here is the presence of charge transfer (CT) states among the low-energy-lying states of the heterodimers. CT states were identified for molecule TP2 for selected geometries at different elongations (SI Table S2). The CT energy levels are affected by the distance; thus, the energy of these excited states increases as the center of mass distance length between TDI and PDI increases. Also for the heterodimers (Figure 6), we find a high coupling regime at short elongation where the chromophores are in close contact and strongly interacting. When the force signals a mechanical deformation, the coupling decreases, and as the molecule is stretched further, the coupling drops to a low coupling plateau. We also find an extra mechanical deformation after the main force peak for both TP2 and TP4 but not for TP3 and TP5. An intermediate coupling region is also seen for the even carbon atoms bridge TPn, but it is not seen for the odd carbon atoms bridges, just like the PPn molecules. In contrast with PPn molecules, all of the heterodimers show a larger coupling variance in the folded region. Specifically, the variance becomes larger as the bridge is longer. In fact, for a longer bridge, there are more degrees of freedom, which allows more conformations to be accessible and thus a larger spread in the coupling.

In conclusion, we have simulated a new class of single-molecule spectroscopy experiments in which force microscopy is used to control the excitonic coupling between chromophores in suitably designed dimers. Specifically, we have demonstrated that the exciton coupling can be varied over a broad range of values (0.02—0.15 eV) by mechanical manipulation of the molecule. The stronger and weaker coupling correspond to different regimes of exciton dynamics and are found in correspondence with the folded and elongated structure of the dimer. These two conformations can also be detected optically (because they behave rather differently as H- and J-aggregates, respectively) and, maybe more remarkably, from the force peak: in all of the systems considered, the switch between high and low coupling regimes corresponds to a strong increase of the force and subsequent drop. Relatively modest, but easy to rationalize, changes are observed when the length of the bridge between chromophores is changed, with a potentially interesting “intermediate” regime found for the −(CH₂)₃− bridge. Most of the findings can be translated to the situation where two chromophores are different and their interaction is probed by the rate of energy transfer. Our findings suggest that a SMFS can be used to explore many subtleties of molecular exciton physics thanks to the potentially very accurate control achievable on the excitonic coupling.

**ASSOCIATED CONTENT**

5 Supporting information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.7b01828.

Computational methods for the simulation of the force spectroscopy and computation of the excitonic coupling, comparison of Coulombic excitonic coupling versus total excitonic coupling, reorganization energy for PDI, PMF of all molecules investigated in this work, representative conformations along the simulated pulling experiment for PPn molecules, histogram of the angles between the transition dipole moments of the PDI units for the PPn systems, simulated absorption spectra for PPn systems, and charge transfer states for TP2 at different elongations (PDF)

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Notes

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We have verified that the variation of the transition dipole moment by performing the calculation with different density functionals is modest with respect to the effect observed. For example, the transition dipole momenta obtained from CAM-B3LYP, LC-PBE0, and LC-BLYP are, respectively, 0.5, 2, and 1% larger than the one obtained with LRC-ωPBEh (the same basis set 6-31G* was used).

Typically, the energy and entropy show more structure than the PMF as the two components partially cancel one another, leading to only modest changes in the PMF. The reason why minima in internal energy U do not necessarily show up as minima in the PMF is because when stabilizing interactions are maximized (leading to a reduced value of U) the range of molecular motion typically decreases, leading to a reduced entropy that partially cancels the stabilization due to interactions.


