This study experimentally evaluates the long-term impact of an early childhood psychosocial stimulation intervention on earnings in a low-income country. Twenty years after the intervention was conducted, we find that the earnings of the stimulation group are 25% higher than those of the control group and caught up to the earnings of a nonstunted comparison group. These findings show that a simple psychosocial stimulation intervention in early childhood for disadvantaged children can have a substantial effect on labor market outcomes and can compensate for developmental delays. The estimated impacts are substantially larger than the impacts reported for the U.S.-based interventions, suggesting that ECD interventions may be an especially effective strategy for improving long-term outcomes of disadvantaged children in developing countries.

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SUPPLEMENTARY MATERIALS

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Materials and Methods
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SOLAR CELLS

Coherent ultrafast charge transfer in an organic photovoltaic blend

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Blends of conjugated polymers and fullerene derivatives are prototype systems for organic photovoltaic devices. The primary charge-generation mechanism involves a light-induced ultrafast electron transfer from the light-absorbing and electron-donating polymer to the fullerene electron acceptor. Here, we elucidate the initial quantum dynamics of this process. Experimentally, we observed coherent vibrational motion of the fullerene moiety after impulsive optical excitation of the polymer donor. Comparison with first-principle theoretical simulations evidences coherent electron transfer between donor and acceptor and oscillations of the transferred charge with a 25-femtosecond period matching that of the observed vibrational modes. Our results show that coherent vibrionic coupling between electronic and nuclear degrees of freedom is of key importance in triggering charge delocalization and transfer in a noncovalently bound reference system.

The currently accepted model for the basic working principle of a bulk-heterojunction organic solar cell (1, 2), comprising a conjugated polymer donor and an electron acceptor material, relies on four elementary steps: (i) photon absorption, creating a spatially localized, Coulomb-bound electron-hole pair (exciton) in the donor phase; (ii) exciton diffusion to the donor/acceptor interface; (iii) exciton dissociation at the interface leading to the formation of a charge-separated state (3, 4), often called charge-transfer exciton or polaron pair; and (iv) dissociation of the polaron pair into free charges and their transport to the electrodes.

In this work, we focused on the dynamics of the primary light-induced steps, (i) and (iii), which lead to a charge-separated state in organic photovoltaic (OPV) materials and represent the key process in OPV cells. Over the past years, charge photogeneration has been investigated in several technologically relevant materials, such as blends of polyphenylene-vinylene (5, 6), polythiophene (7, 8), or low band gap polymers (9, 10) with fullerene derivatives. In all of these systems, it is now accepted that charge separation is an ultrafast process occurring on a sub-100-fs time scale. So far the experimental studies on charge photogeneration in OPV materials have mainly been described within the framework of an incoherent transfer model (11, 12), giving a rate constant for the transfer process. These rate constants may be enhanced by hot exciton dissociation
charge-transfer exciton transitions associated to specific local configurations.

In order to gain insight into the primary photoinduced charge-transfer dynamics of the blend, we performed ultrafast spectroscopic studies on such thin films by using a two-color pump-probe spectrometer providing independently tunable pulses (32). Because the charge-carrier photogeneration in P3HT:PCBM blends is essentially independent of temperature (33), all experiments were performed at room temperature. The overall time resolution of the setup is better than 15 fs. Pump pulses centered at 540 nm resonantly excite the \( \pi-\pi^* \) absorption band of P3HT (30, 34), whereas broadband probe pulses monitor the transient absorption in the blue-to-green wavelength range.

Figure 2A shows a measurement of the pump-induced change in optical transmission \( \Delta T / T \) for the P3HT:PCBM blend as a function of probe wavelength \( \lambda \), and pump-probe delay \( \tau \). A similar measurement for the pristine P3HT film is reported in the supplementary materials. For probe wavelengths between 500 and 525 nm, the signal is in both samples dominated by ground-state bleaching of the optically excited exciton transition in the polymer. In the shorter wavelength range, the dynamics are substantially different. There, the exciton bleaching of the polymer becomes less prominent, and we have, in the blend, access to an additional stimulated emission signal from the fullerene or intermediate states. In this region, the blended sample displayed an additional and fast-decaying component on a 100-fs time scale (supplementary materials), which can be assigned to an ultrafast charge transfer from the polymer to the fullerene. This time scale is in agreement with previous reports on similar blends (5) and with the results of detailed pump-probe measurements covering the probe wavelength range between 550 and 1400 nm. These results (supplementary materials) show that a substantial fraction of all photogenerated excitons in the blend undergo rapid charge separation on a 50- to 70-fs time scale.

For both the pristine P3HT and the blend samples, the \( \Delta T / T \) map (Fig. 2A and fig. S2) shows a pronounced oscillatory contrast throughout the entire visible range. We further analyzed these \( \Delta T / T \) data by taking the Fourier transform of the oscillatory component after subtraction of a slowly varying background. In the 500- to 520-nm wavelength region (Fig. 2, B and C), we observed, for both the polymer and the blend, the characteristic C=C stretching frequency of the polymer (1450 cm\(^{-1}\), corresponding to a vibrational period of 23 fs). For shorter probe wavelengths, the behavior became more complex: In the pristine film we saw almost no contrast, whereas in the blended film we detected a strong oscillatory component at a higher frequency of 1470 cm\(^{-1}\). This frequency corresponds to the pinch mode dominating the Raman spectrum.

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of the PCBM film (33, 36). Also in the 470- to 480-nm probe wavelength range, we found vibrational characteristics of the fullerene. There, we saw a weak vibrational mode at 1289 cm⁻¹, corresponding to the T₃₃(3) mode of PCBM. Control experiments on pristine PCBM films (fig. S3) did not show any evidence of coherence, thus ruling out direct PCBM excitation as a cause for the observed oscillations at 1470 cm⁻¹. These results are difficult to reconcile with an incoherent charge-transfer model, which predicts a gradual and monotonous buildup of charge on the fullerene acceptor on a 100-fs time scale that will not trigger coherent motion on a faster time scale. Also, they cannot be interpreted in terms of an incoherent charge transfer taking place within less than one vibrational period (23 fs) because such a fast transfer is neither seen in the ΔT/T data in the supplementary materials nor consistent with finding essentially the same linewidths in the absorption spectra of the pristine P3HT film and the blend. Instead, they provide evidence for a coherent charge transfer mediated by strong vibronic couplings between polymer and fullerene.

To analyze the experimental observations, we have performed first-principle calculations (25) on the simplest possible model of the experimentally studied thin-film blend, a periodic crystal of charge transfer dimers. PBCBM has been substituted with a C₆₀ molecule, and the alkyl side chains on the polymer have been removed in order to reduce the numerical complexity, checking that this does not affect the ground-state properties of the system. By using density functional theory (DFT) at the local density approximation (LDA) level, we relaxed the ground state of the system and found an equilibrium distance of 3.2 Å between 4T and C₆₀. The Kohn-Sham electron energy levels of the 4T-C₆₀ unit are shown in Fig. 1D together with the electronic structure of the isolated C₆₀ and 4T, all aligned to vacuum. The orbital localization shows a highest occupied molecular orbital (HOMO) with 96% localization on the thiophene chain and a lowest unoccupied molecular orbital (LUMO) almost fully localized on the fullerene. The lowest-lying available single-particle thiophene excitation corresponds to a HOMO-to-LUMO transition with 94% localization on the polymer. Steady-state optical absorption spectra (37, 38) of the blend and the isolated components are depicted in Fig. 1, A and B, respectively. The absorption cross sections of both the isolated moieties and of 4T:C₆₀ are in good agreement with the experimentally observed ones. They consist of two distinct absorption bands, centered at 528 and 354 nm, that correspond to thiophene and fullerene excitations, respectively. This calculation supports the picture of a system composed of moieties that are weakly interacting in their ground states.

TDDFT simulations of the dynamics of the photoexcited 4T:C₆₀ model system were performed by imposing periodic boundary conditions in order to mimic the experimental configuration of a blended thin film. We interrogated the system dynamics by assuming an initial instantaneously excited electronic state corresponding to the removal of an electron from the polymer HOMO and the creation of an electron in the polymer LUMO. We chose as initial condition a Maxwellian distribution of random nuclear velocities to approximate the experimental room-temperature environment. We observed that an electron is transferred to C₆₀ with 60% probability within 97 fs, in good agreement with experimental findings (7, 8). Moreover, the charge-transfer probability, taken as the spatially integrated excess charge density on the C₆₀, oscillated in time with a period of about 25 ± 4 fs (Fig. 3A). This period approximately matches the oscillation frequency observed in the experiments. A useful insight into the charge delocalization mechanism is gained by looking at the first few time-dependent Kohn-Sham eigenvalues above the 4T HOMO (Fig. 3C). The continuous purple line represents the 4T LUMO, occupied at time 0 by one electron removed from the 4T HOMO (purple broken line). Its energy undergoes pronounced oscillations in antiphase with the C₆₀ LUMO. At each crossing of the two levels, the charge density is free to move through the system (Fig. 3C), causing a transient peak in the current flowing between 4T and C₆₀ and back (Fig. 3A). Instead, the current flow is suppressed when 4T and C₆₀ LUMOs are energetically detuned, resulting in a periodic variation of the current flow and thus an oscillatory modulation of amount of charge transferred to the C₆₀ moiety. In the long term, the charge will be localized on the acceptor both by a nuclear rearrangement and by energy dissipation. This regime, however, is out of the scope of the present calculations. Our simulations thus predict that vibronic coupling is necessary for charge transfer to occur and indicate that this coupling is responsible for dynamically driving 4T and C₆₀ LUMOs in resonance, explaining the coherent oscillations of the transferred charge. In fact, the electronic excitation remains fully localized on the polymer when keeping the ions in fixed positions (fig. S4).

The charge separation is further analyzed by examining the time-dependent dipole moment of the system (Fig. 3B). Its z component is oriented along the axis from the polymer to the C₆₀ and oscillates in phase with the displaced charge, whereas the y component shows weakly anticorrelated oscillations along the polymer chain. This again points to vibronic coherence and a periodic charge flow between polymer and fullerene. The dynamics of the charge separation process are nicely visualized by displaying the time evolution of the electronic density projected onto the coupled LUMO orbitals of the blend (Fig. 3, D to F, and movie S1). This charge density is created by photoexcitation at time zero and is initially fully localized on the polymer (Fig. 3D). As the time evolves, the charge density delocalizes between polymer and C₆₀, and the degree of fractional charge on both moieties displays anticorrelated temporal oscillations. At the end of the simulation, it is shared between donor and acceptor (Fig. 3F).

In the simulations, we also analyzed the time-dependent ionic displacements (movie S2) and found that the photoexcitation of 4T promotes vibrational motion of the C₆₀ with similar oscillation period as is found in the charge transfer probability. This is consistent with the experimental observation of collective vibronic coherence of the fullerene triggered by impulsive photoexcitation of the polymer.

Fig. 2. Charge transfer dynamics of the P3HT:PCBM blend. (A) Experimental differential transmission (ΔT/T) map of the P3HT:PCBM blend as a function of probe delay and probe wavelength. The pronounced oscillations in the ΔT/T signal reflect coherent vibrational wave-packet motion initiated by the short pump pulse. (B) Fourier transform spectra of the ΔT/T dynamics of the blend (left) and pristine P3HT (right). The spectral intensity is amplified by a factor of 4 for λ = 498 to 485 nm and by a factor of 20 for λ = 485 to 470 nm. (C) Integrated Fourier transform spectra for λ = 520 to 498 nm (top) and λ = 492 to 485 nm (bottom, dashed lines in (B)) of the blend (black) and pristine P3HT (red). The dashed vertical lines indicate the frequency of the P3HT C=C stretch mode (red) at 1450 cm⁻¹ and pentagonal-pincho mode of the fullerene (black) at 1470 cm⁻¹.
We recently studied the charge-transfer dynamics in a very different system, a supramolecular carotene-porphyrin-fullerene triad (24), a model system for artificial light harvesting. The physical nature of this system, a covalently bound molecular complex in solution, is fundamentally different from the one studied here. Nevertheless, we find similar charge oscillations, with a period of about 30 fs, when studying the charge transfer between porphyrin and fullerene. We believe that the key to the similarity of those values can be found in Fig. 3C. It shows that the energies of the relevant LUMOs of the polymer and fullerene vary in time with a period corresponding to that of the vibrational mode to which the electronic state is strongly coupled. The probability for charge transfer is large whenever the polymer and fullerene LUMOs are transiently brought into resonance. Hence, the amount of transferred charge (Fig. 3A) oscillates at the (average) period of the vibrational mode(s) most strongly coupled to the electronic system.

In case of the P3HT:PCBM blend, these are the C=C stretch mode of the polymer at 1460 cm\(^{-1}\) and the pentagonal pinch mode of PCBM at 1470 cm\(^{-1}\), corresponding to an oscillation period of \(23\) fs. This agrees reasonably well with the period of \(25 \pm 4\) fs that we deduce from Fig. 3. A to C. This period is slightly shorter than the 30 fs that we saw in the case of the triad.

We suggest that the similarity of oscillation periods is a direct consequence of strong vibronic coupling. The time evolution of the charge distribution is modulated with a period matching that of the vibrational modes that are most strongly coupled to the charge excitations. Because all carbon-based organic systems have strong vibrations in the 1000 to 1500 cm\(^{-1}\) range, it is likely to experimentally find oscillation periods between 20 and 30 fs. Our results suggest that, despite the very different microscopic properties of the triad and the P3HT:PCBM blend, the coherent charge-transfer dynamics are in both cases governed by strong vibronic coupling.

A consistent and general picture of the elementary photoinduced charge-transfer process in the P3HT:PCBM blend emerges from our detailed experimental and theoretical results. Optical excitation locally creates an electron-hole pair on the polymer moiety. The strong vibronic coupling between electronic and nuclear degrees of freedom promotes a delocalization of the optically excited electronic wave packet across the interface, both the electronic density and the nuclei display correlated oscillations on the same time scales, which are essential for an ultrafast charge transfer from the donor to the acceptor. The observation of coherent electron-nuclear motion in a noncovalently bound complex, averaging over a macroscopic ensemble of P3HT:PCBM moieties with variable environment and interfaces, is strong evidence for the dominant role of quantum coherences in the early stages of the charge transfer dynamics in this class of OPV materials.

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**Fig. 3. Simulation of the charge transfer dynamics.** (A) Charge-transfer dynamics in a crystal of 4T:C60 aggregates after impulsive 4T excitation at time zero. After 97 fs, the charge-transfer probability from 4T to C60 is 60%. Strong oscillations of the transfer probability, with a period of about 25 ± 4 fs, are the signature of coherent charge-transfer dynamics. (B) Time dynamics of the molecular dipole. The z component, oriented along the axis from the 4T to the C60, oscillates in phase with the displaced charge. (C) Time-dependent Kohn-Sham eigenvalues. The purple lines refer to the 4T HOMO (broken) and 4T LUMO (solid) levels; the green lines to the lowest unoccupied C60 levels, respectively. (D to F) Snapshots of the simulated time evolution of the charge density in the coupled 4T and C60 LUMOs. Initially (D), the charge is completely localized on the 4T chain. As time evolves, it delocalizes between 4T and C60 [(E) 57.3 fs, (F) 98.7 fs]. After 98.7 fs (F), the charge density is shared between 4T and C60.
Amorphous TiO$_2$ coatings stabilize Si, GaAs, and GaP photoanodes for efficient water oxidation

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Although semiconductors such as silicon (Si), gallium arsenide (GaAs), and gallium phosphide (GaP) have band gaps that make them efficient photoanodes for solar fuel production, these materials are unstable in aqueous media. We show that TiO$_2$ coatings (4 to 143 nanometers thick) grown by atomic layer deposition prevent corrosion, have much more positive than the formal potential cause the potential of their valence band edge is significantly improved the stability of Si, GaAs, and GaP photoanodes exhibited continuous oxidation of 1.0 molar aqueous KOH to O$_2$ for more than 100 hours at photocurrent densities of $>30$ milliamperes per square centimeter and $~100\%$ Faradaic efficiency.

**WATER SPLITTING**

Deposition of thin films of Pd (7), Pt (8), Ni (9), or metal-doped SiO$_2$ (10) onto n-type Si or n-GaAs photoanodes yields improved stability under water-oxidation conditions, primarily near neutral pH, as well as in strongly alkaline (9) or acidic (10) media for up to 12 hours. However, these stabilized photoanodes generally exhibit low photovoltages; additionally, the protective metal coating is either too thick to be highly optically transmissive or too thin to afford extended stability during water oxidation, particularly in alkaline or acidic media. Transparent conductive oxide (TCO) coatings on Si and GaAs are not stable in strongly alkaline or acidic media, and also produce low voltages because of defective semiconductor/TCO interfaces. (11, 12) Coatings of Ni islands (9), as well as MnO$_2$ (13) and NiO$_2$ (14) films on Si, have been used to catalyze the oxidation of water and thus provide some degree of stability enhancement. However, such coatings do not enable prolonged operation in alkaline media and/or yield very low photovoltages because of a large density of interface states at the Si/NI interface.

Conformal layers of 2-nm thick TiO$_2$ formed by atomic layer deposition (ALD) have been used to stabilize Si, and in conjunction with an IrO$_2$ catalyst, to effect water oxidation (15). Deposition of such electrically insulating films at larger thickness, to reliably prevent pinholes and thus suppress active corrosion over macroscopic areas, creates a tunneling barrier for photogenerated holes. As this barrier becomes larger, the tunneling mechanism also introduces a large series resistance to a PEC device, degrading its efficiency to low values. Specifically, as the TiO$_2$ thickness was increased, the overpotential for the oxygen-evolution reaction (OER) increased linearly at a rate of $\sim 21$ mV nm$^{-1}$ (16), resulting in an additional voltage loss of $\sim 200$ mV for a 12-nm thick TiO$_2$ overlayer, even at a current density of 1 mA cm$^{-2}$.

We describe a general approach to significantly improve the stability of Si, GaAs, and GaP photoanodes against both photocorrosion and photopassivation for water oxidation in alkaline media (all results reported below are for water oxidation, $E^\circ(\text{O}_2/\text{H}_2\text{O})$ (3). Although many semiconductors, including silicon (Si), gallium arsenide (GaAs), and gallium phosphide (GaP), have valence-band edges at more negative potentials than metal oxides and also typically have optimal band gaps for efficient solar-driven water splitting, these semiconductor materials are unstable when operated under photoanodic conditions in aqueous electrolytes. Specifically, in competition with oxidizing water to O$_2$, these materials either anodically photocorrode or photopassivate (3, 4). Furthermore, passive and intrinsically safe solar-driven water-splitting systems can only be constructed (5) in either alkaline or acidic media, and the development of general strategies to stabilize existing photoelectrode materials under water-oxidation conditions is an important goal.

Various coating strategies have been explored to stabilize semiconductors with optimal band gaps (1.1 to 1.7 eV) for direct water splitting (6).