

## APPLIED PHYSICS

# Band structure engineering in organic semiconductors

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A key breakthrough in modern electronics was the introduction of band structure engineering, the design of almost arbitrary electronic potential structures by alloying different semiconductors to continuously tune the band gap and band-edge energies. Implementation of this approach in organic semiconductors has been hindered by strong localization of the electronic states in these materials. We show that the influence of so far largely ignored long-range Coulomb interactions provides a workaround. Photoelectron spectroscopy confirms that the ionization energies of crystalline organic semiconductors can be continuously tuned over a wide range by blending them with their halogenated derivatives. Correspondingly, the photovoltaic gap and open-circuit voltage of organic solar cells can be continuously tuned by the blending ratio of these donors.

The working principles of semiconductor devices crucially depend on the electronic energy levels of conduction and valence states. This also holds for organic semiconductors, which have recently gained much attention for their application in flexible large-area devices not realizable with traditional inorganic semiconductors. In organic semiconductor devices such as organic solar cells (OSCs), light-emitting diodes (OLEDs), and field-effect transistors (OFETs), an accurate energy-level tuning of electron- and hole-transporting electronic states—represented by the frontier orbitals, the highest occupied (HOMO) and lowest unoccupied molecular orbital (LUMO)—is necessary to optimize device efficiency (1–4). For instance, the relative energy position of the HOMO of the donor and the LUMO of the acceptor material is paramount in OSCs, as it controls the open-circuit voltage (1, 5). Also, the tuning of the energy level alignment at the electrode/semiconductor interface is crucial for efficient charge injection in OLEDs and OFETs, and extraction in OSCs (4, 6–8).

In inorganic semiconductors, band-gap engineering (or more generally, band structure engineering) has opened up a new dimension in device design: By blending materials with different energy levels, it became possible to continuously tune band energies by simply varying the composition of binary, ternary, or quaternary alloys (9–11).

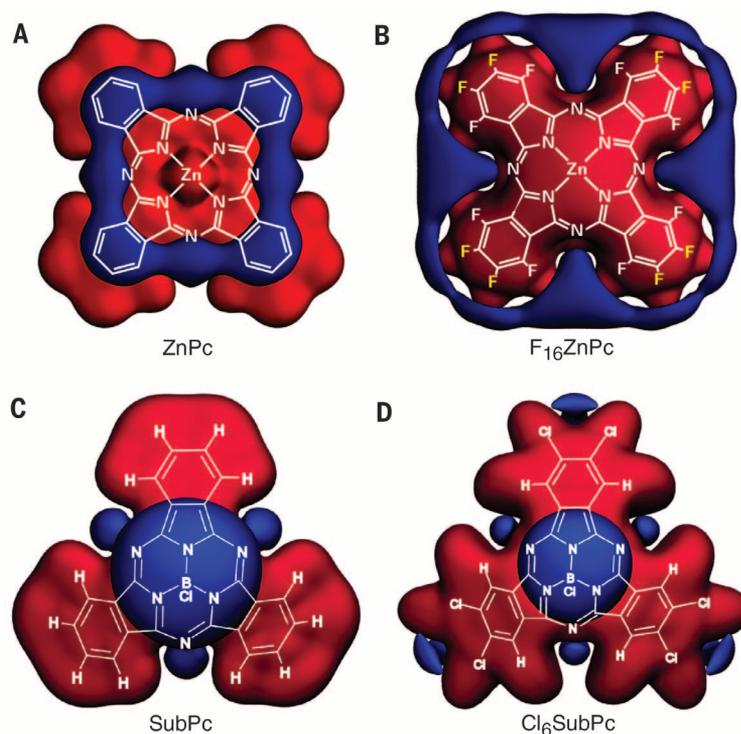
So far, this design principle has not been available in organic semiconductors. Here, the established means of tuning the electronic levels is by

varying the molecular design—for example, by halogenation of organic compounds (12–15). However, such changes in molecular design require a new synthesis and do not provide the same degree of fine-scale tunability obtained by the blending of inorganic semiconductors. Blending of organic molecules has been applied to the active layer in organic solar cells (16, 17) and for interface layers in OLEDs (18, 19). However, in those experiments, only the electronic states of individual molecules

were relevant. Accordingly, blend properties were not used to achieve continuous tuning.

In this study, we show that band structure engineering is possible in organic semiconductors. Despite the strongly localized electronic states of the individual molecules, long-range Coulomb interactions enable continuous tuning in blends (20, 21). As a model material system, we chose zinc phthalocyanine and boron subphthalocyanine chloride (ZnPc and SubPc; Fig. 1A and fig. S3) and their halogenated derivatives (F<sub>4</sub>ZnPc, F<sub>8</sub>ZnPc, F<sub>16</sub>ZnPc, and Cl<sub>6</sub>SubPc; structural formulas in figs. S1 and S3) (22). The energetic, optical, and structural properties of phthalocyanines have already been well investigated in the literature, as also motivated by their good device performance (23).

We first performed ultraviolet photoelectron spectroscopy (UPS) measurements on ZnPc, F<sub>4</sub>ZnPc, F<sub>8</sub>ZnPc, and F<sub>16</sub>ZnPc thin films to obtain measurements of the ionization energy (IE) of neat layers (fig. S1). The IE increases with higher degrees of fluorination from 5.1 eV for ZnPc to 6.75 eV for F<sub>16</sub>ZnPc, whereas the shapes of the spectra remain very similar, as reported previously (24). This increase of IE in fluorinated compounds has been explained by a stabilization of the HOMO level in compounds with electron-withdrawing ligands (13). In ordered thin films, large orientation dependencies of the IE were seen for molecules containing polar bonds (25). For highly ordered thin films of pentacene and perfluoropentacene, this was explained by an orientation dependence of the polarization energy originating from different charge-quadrupole interactions (26, 27).



**Fig. 1. Molecular structural properties of (halogenated) ZnPc and SubPc.** Isopotential surfaces at  $-0.3$  V (blue) and  $+0.3$  V (red) for (A) ZnPc, (B) F<sub>16</sub>ZnPc, (C) SubPc, and (D) Cl<sub>6</sub>SubPc calculated via the DFT method B3LYP/6-311+g(d,p).

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By comparing literature values for the IE of ZnPc (6.3 eV) and  $F_{16}$ ZnPc (7.2 eV) molecules measured by gas-phase UPS with the IE obtained in this study, we can obtain a first estimation of the relaxation energy contribution to the IE of our solid thin-film samples (14). The large difference of  $\sim 0.75$  eV is rationalized by their opposing quadrupole moments (Fig. 1 and table S3).

Salzmann *et al.* (28) showed large shifts in the IE by intermixing of pentacene and perfluoropentacene. However, the IE did not shift linearly with mixing ratio, which was explained by an undesired phase separation in the blend films. In contrast, good intermixing on a molecular scale was shown by x-ray diffraction (XRD) and absorption measurements for a blend of CuPc: $F_{16}$ CuPc (29). As shown by comparison of our XRD results on a ZnPc, an  $F_4$ ZnPc, and a ZnPc: $F_4$ ZnPc (1:1) blend layer (fig. S2) to previous results, the  $\alpha$ -phase crystal structure with an edge-on orientation and fine molecular intermixing in blend layers can be expected (24, 29, 30). Crystallinity of mixed systems and large differences in quadrupole moments of single molecules are key preconditions for tuning energy levels over a wide range (see below).

UPS results on mixed ZnPc: $F_n$ ZnPc layers show a monotonous shift of the HOMO distribution to lower binding energies with increasing ZnPc content, corresponding to a decrease of the IE (Fig. 2, A to C). Whereas the HOMO distributions of neat layers can be fitted by single Gaussian functions, the broader HOMO distributions of the blend layers can only be described by a superposition of two Gaussian peaks (see supplementary materials). The molar ratio of ZnPc and  $F_n$ ZnPc in the blends, obtained from the intensity ratio of fluorine and zinc emission in x-ray photoelectron spectra, was used as the intensity ratio of the peaks.

A detailed analysis of the HOMO peaks in the blends yields several remarkable results. First, the difference of the IE of ZnPc and  $F_n$ ZnPc in the blends is considerably smaller than the difference in the neat films. Second, this difference is constant over a broad range of mixing ratios: The IE of ZnPc and  $F_n$ ZnPc linearly shift to higher (lower) binding energies with increasing content of  $F_n$ ZnPc (ZnPc) in the blends. Hence, the IE in blends of ZnPc with  $F_4$ ZnPc,  $F_8$ ZnPc, and  $F_{16}$ ZnPc can be continuously shifted over a range of 0.5 eV, 0.86 eV, and 1.17 eV, respectively (Fig. 2, D to F, maximum position of Gaussian fits is used), by simply blending these materials. As the linear IE change with mixing ratio is shared by all systems, with larger degrees of fluorination enhancing the slope, a common physical mechanism can already be anticipated.

Density functional theory (DFT) allows estimation of intermolecular interactions along the stacking direction of molecular crystals (31–33). Here, we applied DFT calculations to stacks of  $F_n$ ZnPc molecules with the geometry of the  $\beta$  phase. For model geometries consisting of five stacked molecules, interactions along the stacking direction produce substantial shifts of the HOMO energies. In ZnPc stacks, the inner sites suffer a HOMO destabilization of 0.24 eV on average, whereas in  $F_8$ ZnPc stacks the respective

states are stabilized by  $-0.22$  eV, and the HOMO energies in  $F_4$ ZnPc stacks remain nearly unaffected relative to the gas phase. HOMO shifts on surface molecules of the finite stacks are about half as large.

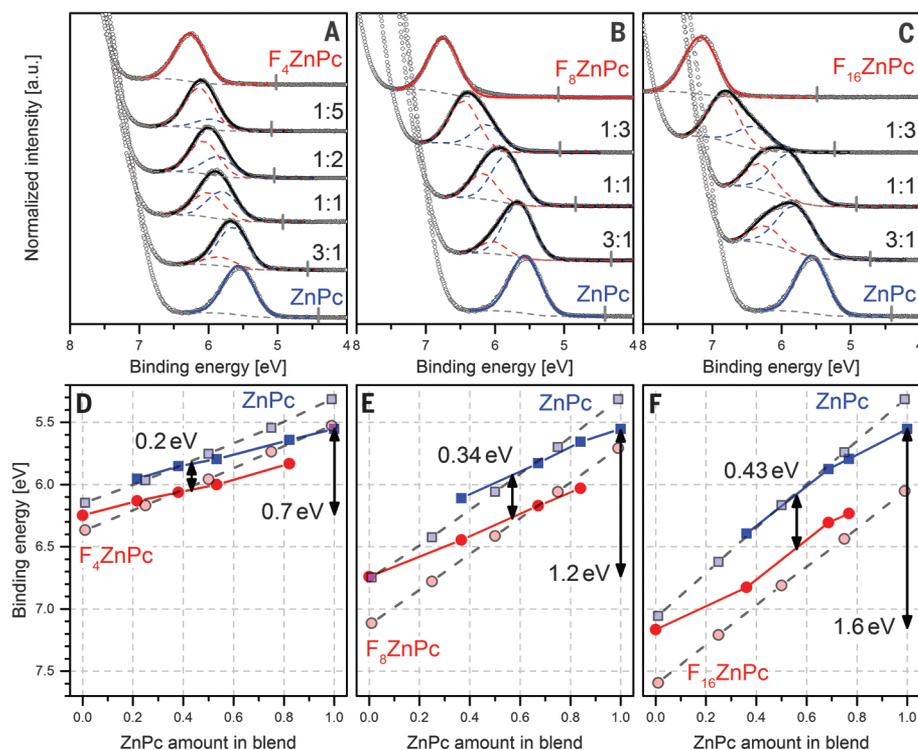
DFT calculations reproduce an essential finding of the UPS measurements (Fig. 3): In mixed stacks of ZnPc and  $F_n$ ZnPc, intermolecular interactions result in two distinct groups of HOMO and LUMO energies, one arising from the fluorinated and one from the nonfluorinated sites, but the splitting between these two groups of orbitals is significantly reduced with respect to the pure phases. The energy difference between the two subgroups reaches a value of 0.20 eV for ZnPc/ $F_4$ ZnPc and of 0.34 eV for ZnPc/ $F_8$ ZnPc, in both cases in excellent agreement with the splitting found in UPS.

The reduced splitting between the orbital energies of fluorinated and nonfluorinated phthalocyanines seems counterintuitive, because any off-diagonal interaction between nondegenerate levels should increase the splitting. Instead, DFT calculations on mixed stacks demonstrate that electrostatic interactions of a molecular orbital with neighboring molecules move the on-site energies of the HOMOs of fluorinated and non-

fluorinated ZnPc toward each other. This effect can be rationalized by accounting for electrostatic interactions of a net charge with quadrupole moments of surrounding molecules.

A deficit of the DFT calculations concerns the overall shift of the HOMO energy arising from fluorination: The UPS measurements reveal a shift of 0.7 eV from ZnPc to  $F_4$ ZnPc, whereas DFT predicts only 0.46 eV. For a more quantitative description of the ionization energies, an explicit account of the excess charge (hole) is required, achieved here via a perturbative embedding procedure applied to large atomistic models (fig. S8; see supplementary materials for simulation details). Such a coarse-grained approach allows the investigation of much larger molecular assemblies.

Our simulations reveal that the microscopic mechanism responsible for the linear behavior is the superposition of quadrupolar molecular fields of two compounds that act on the excess hole. Indeed, in the absence of intermolecular interactions, the density of states (DOS) of the binary mixture would consist only of two peaks corresponding to the ionization energies of ZnPc and  $F_n$ ZnPc in the gas phase. Changes in composition would then only shift the relative height of these



**Fig. 2. Thin-film ionization energies at different mixing ratios.** UPS spectra (gray circles) and fits (solid lines) for mixed blends of (A) ZnPc: $F_4$ ZnPc, (B) ZnPc: $F_8$ ZnPc, and (C) ZnPc: $F_{16}$ ZnPc. In blends, parts of spectra belonging to ZnPc (blue) and  $F_n$ ZnPc (red) are obtained from Gaussian fits with Shirley backgrounds (dashed lines). Mixing ratios of the two compounds in the blends are given by the mass ratios obtained from quartz crystals. Fermi level positions are depicted as short gray solid lines. (D to F) Maximum positions of HOMO distributions of ZnPc (blue squares) and  $F_n$ ZnPc (red circles) over ZnPc content are shown together with simulation results (dashed lines) of the IE of ZnPc (light blue squares) and  $F_n$ ZnPc (light red circles). Simulated onset values are shifted by 500 meV, which is the typical difference between the maximum and the onset of the HOMO peak in the spectra.

peaks, but not their positions. The linear dependence on mixing ratio is thus conditioned solely by the external, solid-state contribution determined by the molecular packing, degree of molecular ordering, and molecular architecture. In fact, ZnPc carries a net-negative out-of- $\pi$ -plane quadrupole component, as opposed to the positive out-of- $\pi$ -plane quadrupole component that characterizes the  $F_n$ ZnPc family (see again the isotopotential maps of ZnPc and  $F_{16}$ ZnPc in Fig. 1, A and B, and table S3). The long-range character of the charge-quadrupole interaction effectively results in a concentration-weighted average over both

contributions, which thus serves as the mechanism for level engineering. Note that the long-range electrostatic contribution is virtually homogeneous across the film. Polarization additionally reduces the level offset between ZnPc and  $F_n$ ZnPc, which accounts for the anomalously small IE offset in the thin film relative to the gas phase. This microscopic view is fostered by the very good agreement between experimentally measured and simulated, composition-dependent IEs (see Fig. 2, D to F, and fig. S9).

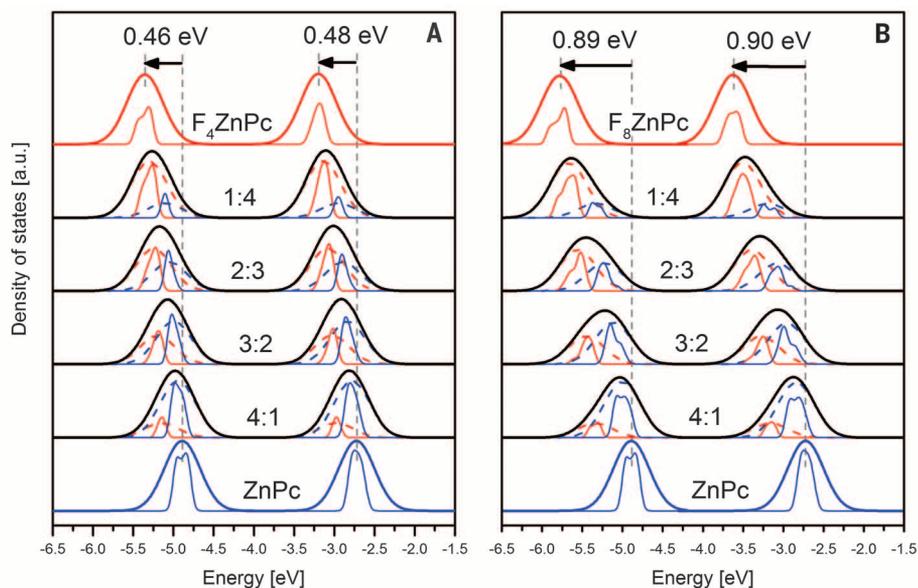
To prove the generality of the observations, we performed UPS experiments on blends of SubPc

and  $Cl_6$ SubPc, a material system with a different symmetry (fig. S3). This system also shows a tuning effect of the ionization energies with mixing ratio and the difference of the IE in the blend is smaller than in neat films. Notably, the IE difference of around 300 meV is similar to the value in ZnPc: $F_8$ ZnPc blends, where the degree of halogenation (i.e., the amount of electron-withdrawing ligands) is comparable. However, the shift of the ionization energies is much smaller than the shift in blends of ZnPc: $F_8$ ZnPc, which already is partly explained by the smaller difference of quadrupole moments of the single molecules (table S3). An orientation deviating from edge-on stacks would decrease the tuning effect even further.

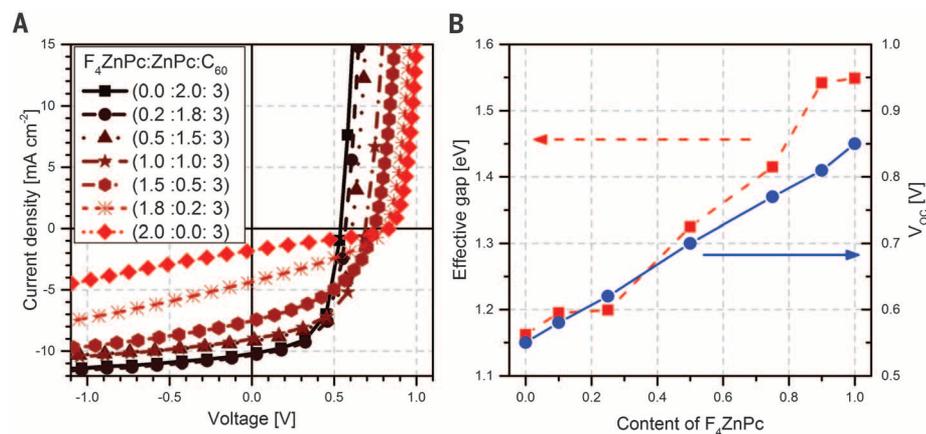
We next address the transport properties of such tunable systems. Previously, a substantial decrease of conductivity in p-doped CBP was seen by admixing molecules with lower ionization energies—that is, by the introduction of traps in the energy gap of CPB (34). Because of the energy distance of the HOMO and LUMO levels between the single molecules in the blends, a negative impact on the charge transport properties might be expected. We obtained mobility data for undoped and temperature-dependent conductivity data for n-doped blends (see supplementary materials). The mobilities slightly decrease for the mixed systems but still allow device application (fig. S4). The room-temperature conductivity increases with mixing ratio from the value of n-doped ZnPc to n-doped  $F_4$ ZnPc (figs. S5 and S6). Accordingly, the activation energy does not show an increase in the blend layers. Obviously, the transport level shifts with the mixing ratio without significantly impairing the transport properties.

To prove that the continuous shift of energy levels can be exploited in devices, we applied the approach in organic solar cells. In previous studies, a correlation of the open-circuit voltage ( $V_{oc}$ ) and the effective gap was measured for several donor-acceptor systems. Here, the effective gap is defined as the difference between the IE of the donor and the electron affinity (EA) of the acceptor (1, 5). As tuning of the IE of the donor by intermixing of ZnPc and  $F_4$ ZnPc is possible, this should equally apply to the effective gap. We chose to study a ternary bulk heterojunction of the two donors with  $C_{60}$  as acceptor. The heterojunction was embedded in a p-i-n-type solar cell (see supplementary materials). The mixing ratio of  $F_4$ ZnPc and ZnPc was varied from pure  $F_4$ ZnPc to pure ZnPc while the  $C_{60}$  content was fixed at 60 weight percent.

Tuning the IE of the donor indeed changes the current-voltage characteristics (Fig. 4A and table S1). The  $V_{oc}$  shifts almost linearly to higher values with increasing  $F_4$ ZnPc content, as observed in earlier studies on other ternary blends (35, 36). The 300-meV shift of  $V_{oc}$  in our solar cells is, however, smaller than expected from UPS measurements on binary ZnPc: $F_4$ ZnPc blends. For that reason, we also performed UPS measurements on ternary blends with varying donor:donor ratio (fig. S9). From pure ZnPc to pure  $F_4$ ZnPc, the IE of the donor shifts to higher binding energies by 700 meV (i.e., the same magnitude as in binary



**Fig. 3. Calculated DOS of the HOMO and LUMO levels.** Mixed stacks of (A) ZnPc: $F_4$ ZnPc and (B) ZnPc: $F_8$ ZnPc consisting of five molecules according to the geometry of  $\beta$ -ZnPc. The results are averaged over all possible orderings of the stacks, convoluted with a Gaussian broadening of 100 meV (thin solid lines) and 500 meV (dashed lines) for ZnPc (blue) and  $F_n$ ZnPc (red). Thick solid lines depict the sum of ZnPc and  $F_n$ ZnPc levels with a broadening of 500 meV.



**Fig. 4. Solar cell performance of ternary blends.** (A) Current density–voltage curves of ternary blends with varied donor composition. (B) Open-circuit voltage ( $V_{oc}$ , blue circles) and effective gap (red squares) obtained by UPS as a function of  $F_4$ ZnPc content.

blends). The IE of the acceptor  $C_{60}$  also shifts to higher binding energies by 300 meV, mirroring the increase in IE that is driven by the change in long-range quadrupolar fields. Assuming a constant distance between the IE and the EA of 2.4 eV for  $C_{60}$  in all ternary blends, the effective band gap for all samples can be calculated (37). The relation of  $V_{oc}$  and the effective gap deviates from a linear correlation only at higher  $F_4ZnPc$  contents (Fig. 4B and table S1).

Tuning of energy levels by superimposing quadrupole fields is expected to work in a variety of semiconducting small molecules and polymers, but a few preconditions appear necessary. Besides the large difference in the magnitude of the quadrupole moments along the thin-film normal, the superposition of their fields must be coherent facilitated by a systematic orientation of both species in the films. A tuning effect can even be realized with constituents of the same polarity, but different orientation in the film, which thus effect a different out-of-plane quadrupole moment. Although the spatial range of this tuning effect and the required degree of molecular intermixing need further investigation, not only bulk tuning but also tuning the energy levels spatially by gradients of the mixing ratios is possible. This may motivate entirely new designs of device architectures for organic semiconductors.

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#### SUPPLEMENTARY MATERIALS

www.sciencemag.org/content/352/6292/1446/suppl/DC1  
Materials and Methods  
Figs. S1 to S11  
Tables S1 to S3  
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#### ASTROCHEMISTRY

## Discovery of the interstellar chiral molecule propylene oxide ( $CH_3CHCH_2O$ )

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Life on Earth relies on chiral molecules—that is, species not superimposable on their mirror images. This manifests itself in the selection of a single molecular handedness, or homochirality, across the biosphere. We present the astronomical detection of a chiral molecule, propylene oxide ( $CH_3CHCH_2O$ ), in absorption toward the Galactic center. Propylene oxide is detected in the gas phase in a cold, extended molecular shell around the embedded, massive protostellar clusters in the Sagittarius B2 star-forming region. This material is representative of the earliest stage of solar system evolution in which a chiral molecule has been found.

The origin of homochirality is a key mystery in the study of our cosmic origins (1). Although homochirality is itself evolutionarily advantageous (2), the mechanism for the selection of one iso-energetic enantiomer over another is uncertain. Many routes to homochirality have been proposed through the amplification and subsequent transfer of a small primordial enantiomeric excess (e.e.). Disentangling these possible mechanisms requires that we understand the potential sources from which an e.e. may arise. The oldest material on which e.e. data have been taken in the laboratory are meteoritic samples (3), yet the provenance of this

e.e. remains a matter of considerable debate (4). Material in molecular clouds from which planetary systems form is processed through circumstellar disks (5) and can subsequently be incorporated into planet(esimal)s (6). Thus, a primordial e.e. found in the parent molecular cloud may be inherited by the fledgling system. Constraining the origin of e.e.s found in meteorites therefore requires the determination of the possible contributions of primordial e.e.s and thus the detection of a chiral molecule in these environments.

For the past 50 years, radio astronomy has been the primary method for studying the gaseous, complex molecular content of interstellar clouds. In this regime, observed spectral features correspond to fine-structure transitions of atoms, or pure rotational transitions of polar molecules, that can uniquely identify their carrier. The observations presented here were taken toward the Sagittarius B2 North [Sgr B2(N)] molecular cloud, the preeminent source for new complex-molecular detections in the interstellar medium (ISM).

Propylene oxide (Fig. 1) was initially detected using data from the publicly available Prebiotic

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Editor's Summary

**Organic solar cells tuned by blending**

Electrical engineers can finetune the energetics of rigid photovoltaics and transistors by blending different semiconducting materials. However, it's hard to apply this tuning protocol to the flexible class of carbon-based semiconductors. Schwarze *et al.* now show that continuous band energy tuning is indeed possible by varying the blend ratios of certain organic phthalocyanines and their fluorinated or chlorinated derivatives (see the Perspective by Ueno). They demonstrated the effect, which they attribute to quadrupolar interactions, in model solar cells.

*Science*, this issue p. 1446; see also p. 1395

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