The catalyst now reported from this group functions in a common organic solvent (pro- 
pylene carbonate) without any further additives or light. It achieves a high turnover num-
ber (the number of times the catalyst molecule performs the reaction before it decom-
poses) of up to 100,000 and a high turnover frequency (the speed of the catalyst cycles) 
of nearly 10,000 hours−1. The catalyst shows high selectivity for H2 formation, whereas the 
rate of the competing HCOOH decomposition pathway to CO and H2O is negligible.

The catalyst consists of an iron cation that is permanently coordinated by four phospho-
rus centers of a tetradentate phosphate ligand, namely tris[(2-diphenylphosphino)ethyl] 
phosphine (PP3). The remaining two coordination sites of the FeII center are occupied by 
the HCOOH substrate and/or product-derived species during the catalytic cycle. The cata-
lyst can be formed in situ from [Fe(BF4)2] and the PP3, ligand under reaction conditions or 
can be added to the reaction mixture in a pre-
synthesized form as [Fe(HPP3)]+. 

Spectroscopic studies and density func-
tional theory calculations suggest two viable pathways for H2 release from HCOOH, both 
of which go through a common Fe-hydride species, [FeH(HPP3)]+. In the first candidate 
catalytic cycle, the Fe-hydride combines with 

formate coordinates to [FeH(HPP3)]+. In the second candidate catalytic cycle, formate coordinates to [FeH(HPP3)]+ to form a neutral [FeH(HCO2)(HPP3)] species. β-hydride elimination and protonation releases CO2 and closes the catalytic cycle after H2 release. The Fe center remains exclu-
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To tap the full potential of HCOOH as a H2 storage material and maintain the “green” 
nature of H2, HCOOH must be produced in large quantities in environmentally benign 
processes (12) (see the figure). On one hand, HCOOH can be considered a solar fuel when 
it is obtained from biomass fermentation and processing. On the other hand, the direct pro-
duction of HCOOH from H2 and CO2 would not require cultivable land and would also be 

preferable for scalability reasons. Although homogenous hydrogenation of CO2 (13) and 
electrochemical CO2 reduction (14) are cur-
rently very active research fields, molecular 
catalysts that are based on abundant metals 
remain scarce also for this reaction (15).

The H2 that is to be stored as HCOOH 
has to be produced from carbon-free sources, 
preferably in a sustainable manner. Currently, 
>95% of H2 is produced either from oil by steam reforming or from coal by coal gasifi-
cation. The direct conversion of solar energy 

to H2, potentially through artificial photosyn-
thetic reaction schemes, would provide such 
an option (16, 17). It will only be in connec-
tion with equally sophisticated catalysts for 
solar H2 generation and CO2 reduction or hydrogenation that the catalyst by Boddien 
et al. will find its place in a hydrogen economy.

References and Notes
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PERSPECTIVES

Generating Helices in Nature
Yoel Forterre1 and Jacques Dumais2

M

acroscopic helical structures 

formed by organisms include sea-

shells, horns, plant tendrils, and 

seed pods (see the figure, panel A). The heli-

ces that form are chiral; like wood screws, 

they have a handedness. Some are helicoids, 
twisted helices with saddle-like curvature and 
a straight centerline; others are cylin-
drical helices with cylindrical curvature and a 

helical centerline. Studies of the mechanisms 

underlying the formation of helicoid or helical 

ribbons and of the transitions between these 

structures (1–4) have left an important ques-
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metrical features interact to create a diversity of 

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Armon et al. (5) explore the rich phenome-
nology associated with slender strips made of 

mutually opposing “molecular” layers, taking 

a singular botanical structure—the Bauhinia 

seed pod—as their inspiration. They show 

that a single component, namely a flat strip with a 
saddle-like intrinsic curvature, is sufficient to 
generate a wide variety of helical shapes.

To illustrate Armon et al.’s findings, we use 
the same paper models used by botanists to 
explain, more than 100 years ago, the helical 
shape of the Bauhinia pod and related plant 
structures (6, 7). The fibers within a sheet of 

paper tend to be aligned parallel to each other 
and give the sheet anisotropic material prop-
erties—when dipped in water, the sheet of 
paper swells preferentially in the direction 

transverse to the fibers. By stacking two such 

sheets back-to-back but with their fiber direc-
tions at right angles (cross-grained)—see the

MATERIALS SCIENCE
Generating Helices in Nature
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figure, panel B), a bilayer is formed that, once swelled in water, tries to bend in two opposite and perpendicular directions.

Strips cut out of this material closely mimic many plant structures and lead to a rich phenomenology of shapes, depending on the orientation and width of the strip. For a wide strip cut along one of the principal fiber directions (i.e., 0° or 90°), pure bending occurs either along or transverse to the long axis of the strip. For a strip cut inclined with respect to the fiber direction, chiral shapes, either helicoids or helical ribbons, are formed.

The bending of an initially flat strip into a saddle-like configuration cannot be achieved without stretching the sheet; this means that elastic energy is stored in the system. To find the equilibrium shape of such “mechanically incompatible” strips, Armon et al. developed a general and elegant mathematical framework where the configuration of the strip is fully characterized by two two-dimensional tensors (which are mathematical generalizations of vectors): a curvature tensor describing the local curvature of the sheet, and a metric tensor describing the distance between points on the surface of the strip. They then minimize the total elastic energy of the strip, that is, the sum of bending and stretching energy.

Armon et al.’s main result is that the variety of helical shapes shown in the figure, panel C, are controlled by only two dimensionless parameters: The direction θ between the strip’s long axis and the directions of intrinsic curvature (i.e., the fiber directions), and the dimensionless width \( \bar{w} = w(\kappa_0/t)^{1/3} \), where \( w, t, \) and \( \kappa_0 \) are the width, thickness, and intrinsic curvature of the strip, respectively. For \( \theta = 45° \), “narrow” strips (small width, large thickness, and small intrinsic curvature) form helicoids, whereas “wide” strips (large width, small thickness, and large intrinsic curvature) form helical ribbons.

Experiments performed on elastic bilayers composed of stretched latex sheets quantitatively agree with the model predictions for a wide range of parameters. In particular, the pitch and radius of the helices are predicted, as well as the smooth transition between helicoids and helical ribbons. Interestingly, in the wide-strip regime, two states having the same elastic energy coexist for a given value of θ and \( \bar{w} \) (see the figure, panel C). To pass from one state to another, elastic energy is stored slowly, and once an energy barrier is overcome, it is rapidly released. This snap-through mechanism in bodies with opposite intrinsic curvatures is found in some plants to speed up their movement (8) and is used in deployable structures such as tape springs (9).

Armon et al.‘s study accompanies several works published in the past year on helical shape formation in different fields and contexts that, together, underlie the robustness and universality of their simple mechanism. For example, Sawa et al. (10) performed experiments on thin strips made of twist-nematic elastomers (soft materials possessing both the elastic properties of rubber and the orientational properties of liquid crystals) and showed a similar transition between helicoid and helical ribbons as the system width increased. To model their system, they introduced a term in the elastic energy accounting for a spontaneous twist at the molecular scale—an approach frequently used to describe chiral biological macromolecules and membranes. Chen et al. (11) developed a framework to predict the helical shape of narrow ribbons with arbitrary intrinsic curvature, taking surface stress anisotropy as the main ingredient of anisotropy.

The generic approach of Armon et al. should be applicable to all of these different situations, as it does not rely on the specific knowledge of the microscopic interaction. The Bauhinia seed pod and its mechanical analogs clearly show how chiral shapes can emerge from global geometrical constraints without bulk chirality at the microscopic level. In the paper bilayers, the hand edness of the helix is determined by the orientation of the principal fiber directions with respect to the long axis of the strip, and can be reversed by simply cutting the strip at an angle below or above 90°. That this versatility can be achieved with a mere piece of paper should convince anyone of the power of this approach to build materials with exciting new properties.

References