

the experiment of Kawakami *et al.*? Some participants hearing the racist comment might identify with their own racial group, feeling emotions of pride and smug superiority to blacks. (Such an identification is no doubt what a real-life originator of a racist comment would be trying to elicit.) A second possibility, predicted by most forecasters, involves identification as a liberal, egalitarian person and perception of the racist as a violator of important norms of tolerance (or, at the very least, suppression of inappropriate speech). Such identification triggers distress and outrage and may also result in feelings of empathy toward the innocent black target of the comment (8).

A third potential identity, not tied to membership in any particular social group, is simply that of an experimental participant. The “research participant” identity in experimental situations is highly constraining. In the famous obedience study by psychologist Stanley Milgram, for example, people hated delivering presumed electric shocks to the “learner” as they were instructed, but most found it impossible to tell the experimenter that they refused to do so (9). The constraints of being in an experiment are very real to people experiencing the situation but are much less salient for forecasters, who therefore mis-

predict their reactions (4). From the perspective of an experimental participant, the racist comment is merely an unusual occurrence in the experimental context, able to be reinterpreted or minimized, and so eliciting little negative emotion or action. This appears to be the identity taken on by most experiencers in the study of Kawakami *et al.* Thus, it is not so much that forecasters mispredicted the emotional reactions that experiencers would feel, as that they mispredicted the identity that would be most salient in the actual situation. This represents a failure of identity forecasting rather than affective forecasting.

These results illustrate the flexibility of our social identities in the face of fluid social contexts. The Kawakami *et al.* study results suggest that the racist remark becomes the focal feature of the situation for some people, but it is easily dismissed as an oddity for individuals who categorize themselves in a different way. The results also show the power of categorization to determine whether someone takes on a proud racial identity that derives esteem from seeing blacks as inferior or a more egalitarian identity that leads to distress at a racist comment. We are not prisoners of our group memberships, inevitably drawn to ethnocentric thinking that glorifies our own racial or other

ingroups and derogates outgroups. Instead, our flexible social categorizations can lead us to reject fellow group members who violate norms of tolerance and egalitarianism, and to avoid—and perhaps, in an ideal world, even to confront—those individuals (10). And it is often our emotional reactions that first clue us in, sometimes to our surprise, to the identity that is guiding our perceptions and reactions in a given situation.

#### References and Notes

1. K. Kawakami, E. Dunn, F. Karmali, J. F. Dovidio, *Science* **323**, 276 (2009).
2. D. T. Gilbert, E. C. Pines, T. D. Wilson, S. J. Blumberg, T. P. Wheatley, *J. Pers. Soc. Psychol.* **75**, 617 (1998).
3. T. D. Wilson, D. T. Gilbert, in *Advances in Experimental Social Psychology*, M. Zanna, Ed. (Elsevier, San Diego, CA, 2003), pp. 345–411.
4. E. W. Dunn, T. D. Wilson, D. T. Gilbert, *Pers. Soc. Psychol. Bull.* **29**, 1421 (2003).
5. D. M. Mackie, E. R. Smith, D. G. Ray, *Soc. Pers. Psychol. Compass* **2**, 1866 (2008).
6. E. R. Smith, C. R. Seger, D. M. Mackie, *J. Pers. Soc. Psychol.* **93**, 431 (2007).
7. M. B. Brewer, J. G. Weber, *J. Pers. Soc. Psychol.* **66**, 268 (1994).
8. E. Subasic, K. J. Reynolds, J. C. Turner, *Pers. Soc. Psychol. Rev.* **12**, 330 (2008).
9. S. Milgram, *J. Abnorm. Soc. Psychol.* **67**, 371 (1963).
10. C. W. Leach, A. Iyer, A. Pedersen, *Pers. Soc. Psychol. Bull.* **32**, 1232 (2006).
11. Supported by NSF (grant BCS-0719876).

10.1126/science.1168650

## CHEMISTRY

# Extending Polymer Conjugation into the Second Dimension

Dmitrii F. Perepichka<sup>1,2</sup> and Federico Rosei<sup>2,3</sup>

Organic materials are typically insulators, but polymers with backbones containing extended networks of conjugated  $\pi$  bonds can exhibit semiconducting behavior. Conjugated polymer semiconductors are used as active materials in optoelectronic devices, particularly in applications in which high speed is not critical. Their advantages versus traditional inorganic materials include simpler and cheaper processing and tunable properties. Yet the trade-off is a lower mobility of charge carriers in these more disordered systems. Conjugated polymers are

one-dimensional (1D) chains, so the charge carriers are slowed down as they hop between chains and across disordered chain fragments. Efforts are under way to create polymers with conjugation in two dimensions, because they may have enhanced carrier mobility or other favorable properties.

The extremely high carrier mobility of graphene—a completely conjugated single sheet of graphite (1, 2)—suggests that high mobilities might be achieved in 2D organic polymers. Although their carrier mobilities would likely be lower than for graphene, the greater variety of possible structures could allow for tuning of electronic properties and may confer advantages in processing. For 1D polymers, mobilities can be comparable to that of amorphous silicon [ $\sim 1$  square centimeter per volt per second ( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ )] but are still well below that of surface-bound graphene (which can be as high as 20,000

Crystal surface templates may improve the electronic properties of conjugated polymers by linking them into two-dimensional networks.

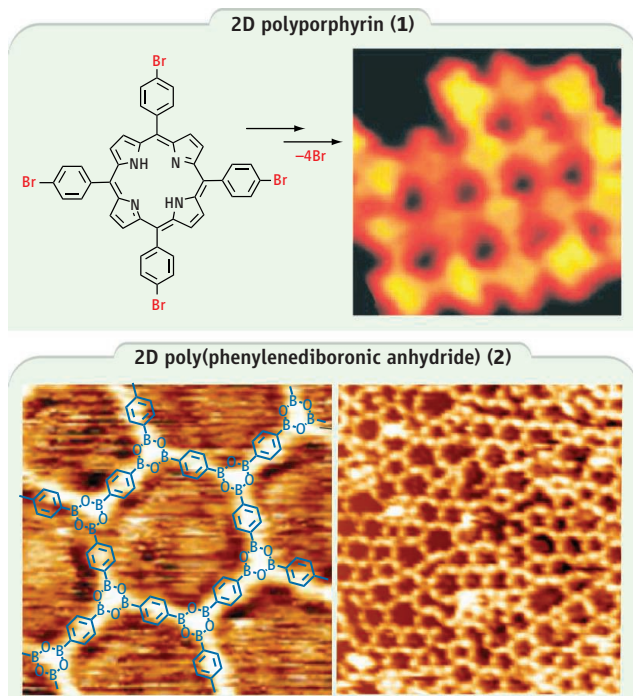
$\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ ). Some 2D polymers might also have zero band gap and potentially exhibit metallic conductivity.

The properties of 2D conjugated polymers have been explored theoretically for more than two decades (3–5). However, experimental efforts aimed at creating and characterizing such materials are more recent. The challenges include the design of properly functionalized monomers that can react in two independent directions without sterically hindering each other, and identifying a suitable template to guide the formation of a continuous 2D network. Because rigid and planar 2D conjugated polymers will certainly be insoluble, classical solution polymerization and characterization techniques are not likely to be suitable. Atomically flat single-crystal surfaces can act as templates to confine polymerization reactions epitaxially in two dimensions and enable in situ characterization

<sup>1</sup>Department of Chemistry, McGill University, 801 Sherbrooke Street West, H3A 2K6 Montréal, Québec, Canada. <sup>2</sup>Centre for Self-Assembled Chemical Structures, <sup>3</sup>Institut National de la Recherche Scientifique, Énergie, Matériaux et Télécommunications, Université du Québec, 1650 Boulevard Lionel Boulet, J3X 1S2 Varennes, Québec, Canada. E-mail: dmitrii.perepichka@mcgill.ca; rosei@emt.inrs.ca

with methods such as scanning tunneling microscopy (STM).

Epitaxial surface polymerization was initially used to create 1D polymers. Building on pioneering studies from the 1970s (6), Okawa and Aono (7) and Miura *et al.* (8) reported the topological polymerization of self-assembled molecular networks of diacetylene monomers on graphite. They used either voltage pulses from the STM tip or ultraviolet light to create 1D polydiacetylene lines that were held together laterally by nonconjugated linkages.



**Conjugated polymers in the plane.** Chemical structures and STM images of (top) polyporphyrin **1** [reproduced from (12), with permission] and (bottom) poly(phenylenediboronic anhydride) **2** [reproduced from (18), with permission] formed on gold surfaces.

More recent studies include the electro-oxidative epitaxial polymerization of thiophene units on iodine-covered gold surfaces (9, 10) and the addition polymerization of tetra-azapyropyrene on copper (11).

Grill *et al.* (12) extended surface reactions to synthesize 2D conjugated networks by annealing tetrakis(bromophenyl)porphyrin on a gold single crystal, which acts as a passive template. The exceptionally high stability of the porphyrin core allows the monomer to be heated above 330°C, where the dissociation of the weakest C–Br bonds results in reactive phenyl radicals. Under ultrahigh-vacuum conditions, these radicals couple to each other to form a square-lattice 2D poly(tetrakisphenyleneporphyrin) **1** (see the figure, top panel). Other groups have polymerized structurally similar porphyrin

monomers (13, 14), but the resulting 2D polymers were not conjugated.

Adapting solution polymerization reactions to single-crystal surfaces poses many challenges; the monomer reactivity can be affected, and reactions are more limited by diffusion. Indeed, surface-confined polymerizations have yielded oligomers that were at most several tens of units large. The “chain-end” effects that limit the properties of shorter 1D conjugated oligomers are likely to be even more detrimental for 2D structures.

The formation of defect-free continuous polymer sheets will require either a topological polymerization reaction in a preordered monomer or a self-repair mechanism, in which the mislinked units can dissociate and reconnect to converge into the most thermodynamically stable structure. However, reactions that reversibly form a covalent bond are rare. One possibility is linking an aldehyde (–CHO) and an amine (–NH<sub>2</sub>) with an imine bond (–CH=N–). The by-product of the reaction (water) can hydrolyze the imine bond, driving the reaction backward and facilitating self-repair.

Using this approach, Weigelt *et al.* have linked aromatic trialdehydes with aliphatic diamines into a 2D imine polymer (15). In this case, aliphatic chains break the conjugation and yield flexible and poorly ordered polymers. Côté *et al.* (16) have shown that heating phenylene-1,4-diboronic acid in a closed container leads to a crystalline boronic anhydride polymer consisting of layers of 2D covalent networks (17). Zwaneveld *et al.* performed the same reaction in monolayers on the Au(111) surface and imaged the resulting 2D “honeycomb” networks by STM (see the figure, bottom panel) (18). However, under the ultrahigh-vacuum conditions used in (15) and (18), the water by-product immediately desorbs, disabling the reverse self-repair reactions and leading to high defect densities. Performing such reactions at a solid-liquid interface might yield better ordered structures.

The surface polymerization reactions described above have all been performed on conducting substrates, but the useful proper-

ties of 2D conjugated polymers would mainly be exploited on insulating surfaces (for example, gate dielectrics in transistors). It might be possible to use insulating surfaces directly as templates. Alternatively, exfoliation of the 2D polymer from a substrate or sacrificial oxidation of the top layer of a substrate (to create an insulating oxide interlayer) can be explored.

The use of 2D polymers as active components in devices will require new strategies for their synthesis over large areas and subsequent manipulation. If these efforts are successful, 2D conjugated polymers could have improved functionalities over conventional conjugated polymers, for example, by achieving true metallic behavior (zero band gap), ambipolarity of charge carriers, and higher carrier mobility. Their application in current technologies could lead to faster and less dissipative organic transistors and more efficient sensors. In the future, 2D polymerization on surfaces could enable the bottom-up construction of nanoelectronic circuits that are “one molecule” in size.

#### References and Notes

- D. Li, R. B. Kaner, *Science* **320**, 1170 (2008).
- Large polyaromatic hydrocarbons synthesized by conventional solution methods as well-defined oligomers can be considered nanographene sheets (19).
- F. K. Abraham, D. R. Nelson, *Science* **249**, 393 (1990).
- R. H. Baughman, H. Eckardt, M. Kertesz, *J. Chem. Phys.* **87**, 6687 (1987).
- K. Tanaka, N. Kosai, H. Maruyama, H. Kobayashi, *Synth. Met.* **92**, 253 (1998).
- B. Tieké, G. Wegner, D. Naegelé, H. Ringsdorf, *Angew. Chem. Int. Ed.* **15**, 764 (1976).
- Y. Okawa, M. Aono, *Nature* **409**, 683 (2001).
- A. Miura *et al.*, *Langmuir* **19**, 6474 (2003).
- H. Sakaguchi, H. Matsumura, H. Gong, *Nat. Mater.* **3**, 551 (2004).
- H. Sakaguchi, H. Matsumura, H. Gong, A. M. Abouelwafa, *Science* **310**, 1002 (2005).
- M. Matena, T. Riehm, M. Stöhr, T. A. Jung, L. H. Gade, *Angew. Chem. Int. Ed.* **47**, 2414 (2008).
- L. Grill *et al.*, *Nat. Nanotechnol.* **2**, 687 (2007).
- J. Michl, T. F. Magnera, *Proc. Natl. Acad. Sci. U.S.A.* **99**, 4788 (2002).
- M. I. Veld, P. Iavicoli, S. Haq, D. B. Amabilino, R. Raval, *Chem. Commun.* **2008**, 1536 (2008).
- S. Weigelt *et al.*, *Angew. Chem. Int. Ed.* **47**, 4406 (2008).
- A. P. Côté *et al.*, *Science* **310**, 1166 (2005).
- Although the conjugation can formally extend through boronic anhydride (via the  $>B^{(+)}-O^{(-)}$  resonance structure), it will be quite weak.
- N. A. A. Zwaneveld *et al.*, *J. Am. Chem. Soc.* **130**, 6678 (2008).
- K. Müllen, J. P. Rabe, *Acc. Chem. Res.* **41**, 511 (2008).
- We acknowledge funding from le Ministère du Développement Économique, de l'Innovation et de l'Exportation (Quebec), the Natural Sciences and Engineering Research Council (Canada), the Petroleum Research Fund (American Chemical Society), the Air Force Office of Scientific Research, and the Asian Office of Aerospace Research and Development (U.S.A.). D.F.P. is a Dupont Young Professor. F.R. is grateful to the Canada Research Chairs program for partial salary support.

10.1126/science.1165429