

- [14] Our acid titration studies suggest a pK_a of around pH 4.5 for the poly(4-vinylpyridine) homopolymer.
- [15] We have carried out control experiments using linear (non-cross-linked) P4VP/SiO₂ nanocomposite particles as an emulsifier. Dissolution at low pH causes a significant increase in solution viscosity, which is detrimental to efficient macroscopic phase separation. Thus a low degree of crosslinking leads to a significant enhancement in demulsification efficiency.
- [16] B. P. Binks, J. H. Clint, *Langmuir* **2002**, *18*, 1270.
- [17] In the work of Amalvy et al. [6,7] and Read et al. [8], the sterically stabilized polystyrene latex actually only acts as a *pH-dependent*, rather than a *pH-responsive* particulate emulsifier. The pH of the initial solution dictates whether or not a stable emulsion is obtained. However, once the latex particles are actually adsorbed at the oil-water interface, desorption *cannot* be achieved by simply switching the solution pH. This is contrary to some of the discussion in these earlier papers and the true situation has only become clear to us very recently. We have published a correction to previous work [8] in *Langmuir* to clarify this important distinction (E. S. Read, S. Fujii, J. I. Almavy, D. P. Randall, S. P. Armes, *Langmuir* **2005**, *21*, 1662). Thus these nanocomposite microgels are the first example of a genuinely pH-responsive particulate emulsifier.

Conductive Hybrid Films of Polyarylamine Electrochemically Oxidized with the Molecular Nanomagnet [Mn₁₂O₁₂(H₂O)₄-(C₆F₅COO)₁₆]**

By Henk J. Bolink,* Eugenio Coronado,*
Alicia Forment-Aliaga, and Carlos J. Gómez-García

Hybrid organic-inorganic materials constitute an active focus of research in materials science. Indeed, the hybrid approach can lead to materials with multifunctional properties^[1] or to materials where their components interact in a synergic way leading to improved properties.^[2] One type of these hybrid materials is based on conducting organic polymers combined with inorganic components which act as electroactive, photoactive, or catalytic agents.^[3] Most conducting organic polymers are based on conjugated organic polymers that are chemically oxidized. These electrochemically oxidized (or doped) polymers are usually insoluble in common solvents,

which makes the processing of these materials difficult. Processable conjugated conducting polymers, such as poly(3,4-ethylenedioxythiophene) (PEDOT) and polyaniline, are based on semi-stable dispersions.^[4,5]

A completely soluble, although less conductive, class of semiconducting organic materials is based on poly(arylamines). In these systems, the arylamines are either covalently connected to form soluble macromolecules (for example, poly[*N*-vinylcarbazole]) or are dispersed in electronically inactive polymers to yield molecularly dispersed polymers (MDPs).^[6] These materials are soluble in common solvents, easy to process into thin films, and widely used in photocopiers and laser printers. More recently, arylamines were used as hole-transporting units in the photoactive layer of organic light-emitting diodes (OLEDs) and organic solar cells.^[7,8] The conductivity of arylamine-containing polymers, however, is in general too low (in the range of 10⁻¹²–10⁻⁹ S cm⁻¹) for applications where large current transport is required, such as in charge-injection layers in OLEDs and organic solar cells. It would be beneficial for the operation of an OLED to have molecules acting at the same time as the charge-injection and hole-transport entities, as this feature should lower the driving voltage of the device.^[9,10]

A possible approach to increasing the conductivity of these systems consists of increasing the amount of free carriers. This can be achieved by oxidizing the arylamines with strong oxidant molecules such as ClO₄⁻ and AgSbF₆.^[11–13] In these oxidized materials the conductivities increase substantially, up to 10⁻⁵ S cm⁻¹, but are still too low for applications as charge-injection layers. Recently, conductivities as high as 0.1 S cm⁻¹ have been obtained using AgSbF₆ to oxidize the soluble arylamine polymer poly(*N,N'*-diphenyl-*N,N'*bis(4-hexylphenyl)-[1,1'-biphenyl]-4,4'-diamine) (pTPD; Fig. 1, right), allowing the use of these materials as charge-injection layers in OLEDs and organic solar cells.^[14] Notice that pTPD is depicted having *N,N'*-diphenyl-*N,N'*bis(4-hexylphenyl)-[1,1'-biphenyl]-4,4'-diamine (hTPD) as the monomer unit, which resembles very closely the well-known aromatic amine, *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD, Fig. 1) used as a transport molecule in MDPs. In pTPD, the arylamine units are chemically linked to each other; however, due to the angle between adjacent phenyl rings, the conjugation is limited and does not extend significantly along the chain direction.

With the aim to incorporate inorganic molecules with additional properties into a semiconducting polymer, we have used the dodecamanganese metal complex [Mn₁₂O₁₂(H₂O)₄(C₆F₅COO)₁₆] (abbreviated as Mn₁₂PhF₅) (Fig. 1, left) as an oxidant for pTPD. This molecular compound belongs to an extensive family of magnetic complexes, known as the Mn₁₂ family, which are derivatives of [Mn₁₂O₁₂(H₂O)₄(CH₃COO)₁₆] (Mn₁₂ acetate).

From a physical point of view, these compounds exhibit extraordinary magnetic properties. In fact, they behave as magnets at low temperatures, showing quantum-tunneling effects due to their nanometer scale.^[15] Therefore, these nanomagnets may be

[*] Dr. H. J. Bolink, Prof. E. Coronado, Dr. A. Forment-Aliaga, Dr. C. Gómez-García
Institute of Molecular Science, University of Valencia
Dr. Moliner 50, E-46100 Burjassot, Valencia (Spain)
E-mail: henk.bolink@uv.es; eugenio.coronado@uv.es

[**] We thank George Malliaras for the supply of the interdigitated electrodes and for stimulating discussions. This work has been supported by the European Union (MOLNANOMAG and QUEMOLNA networks), Generalitat Valenciana, and by the Spanish Ministry of Education and Science (Projects MAT2001–3507 and MAT2004-03849). H. J. B. acknowledges the support of the Program Ramon y Cajal of the Spanish Ministry of Education and Science.

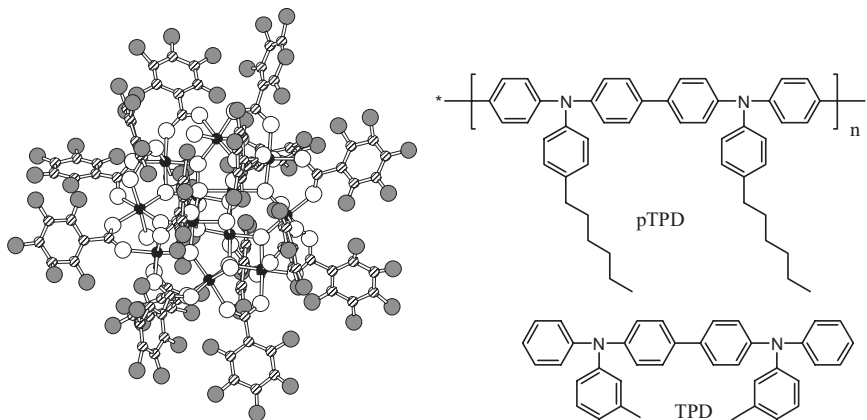


Figure 1. Molecular structure of Mn₁₂PhF₅ functionalized with pentafluorophenyl groups (atoms represented are Mn, black; F, gray; C, dashed gray; O, white), poly(*N,N'*-diphenyl-*N,N'*-bis(4-hexylphenyl)-[1,1'-biphenyl]-4,4'-diamine) (pTPD) and *N,N*-diphenyl-*N,N'*-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD).

useful for preparing high-density magnetic memories and quantum-computing devices.^[16] From a chemical point of view, these compounds are neutral mixed-valence complexes formed by a metal core of four Manganese(IV) atoms and eight Manganese(III) atoms connected by oxo and carboxylate ligands; they can easily be reduced by one or two electrons to yield the corresponding anion complexes. In view of these redox properties, Mn₁₂ complexes may be used to oxidize aromatic amines. The resulting hybrid can also be of interest to study how the environment around a Mn₁₂ cluster affects the magnetic properties of these clusters. In this context, we have chosen a Mn₁₂ derivative functionalized with pentafluorophenylcarboxylate groups, C₆F₅COO⁻, which are more easily reduced than the acetate derivative due to the electron-withdrawing properties of the fluorine atoms. In this work, we report the preparation and properties of this kind of hybrid material.

The electrochemical properties of the pTPD were determined using cyclic voltammetry. Two reversible oxidation peaks are clearly observed in the cyclic voltammogram of pTPD in Figure 2a. The first oxidation peak is observed at 0.28 V, close to that observed for tritolylamine (0.32 V), the basic chemical building block of the pTPD polymer. However, in pTPD there is a second oxidation potential (0.53 V) which appears at the same voltage as the second oxidation peak of the TPD. Therefore, although the magnitudes of the first and second oxidation waves are not of equal intensity, the elementary electronic unit of the pTPD is not a single triphenylamine unit but is better represented by the dimer (hTPD). The reduction potentials of the Mn₁₂PhF₅ complex (0.64 V and 0.46 V versus ferrocene)^[17] are sufficiently high to oxidize pTPD, allowing the creation of free carriers in the semiconducting polymers. In view of the reduction potentials of Mn₁₂PhF₅, it is conceivable that one cluster can accept two electrons from the TPD units.

Indeed, upon addition of small amounts of Mn₁₂PhF₅ to a diluted chlorobenzene solution containing pTPD, the pTPD was

spontaneously oxidized. This partially oxidized polymer remained completely soluble, allowing for easy processing into thin films. Transparent films with thicknesses between 20 and 200 nm were spin-coated from solution. These films had an additional absorption peak with a maximum around 500 nm ($\lambda_{\text{max}} = 495 \text{ nm}$), typical for arylamine radical cations, that increased when the amount of Mn₁₂PhF₅ increased. Notice that the obtained films remained completely transparent up to a Mn₁₂PhF₅/pTPD ratio of 1:2, indicating that no phase separation occurred on a submicrometer scale and that the films were homogeneous.

The magnetic properties of these films are reported in Figure 3 and are compared to those of crystals of [Mn₁₂O₁₂-(H₂O)₄(C₆F₅COO)₁₆].

The typical behavior for a single molecule magnet is observed, with frequency-dependent in-phase (χ') and out-of-phase (χ'') alternating current (AC) susceptibility signals.

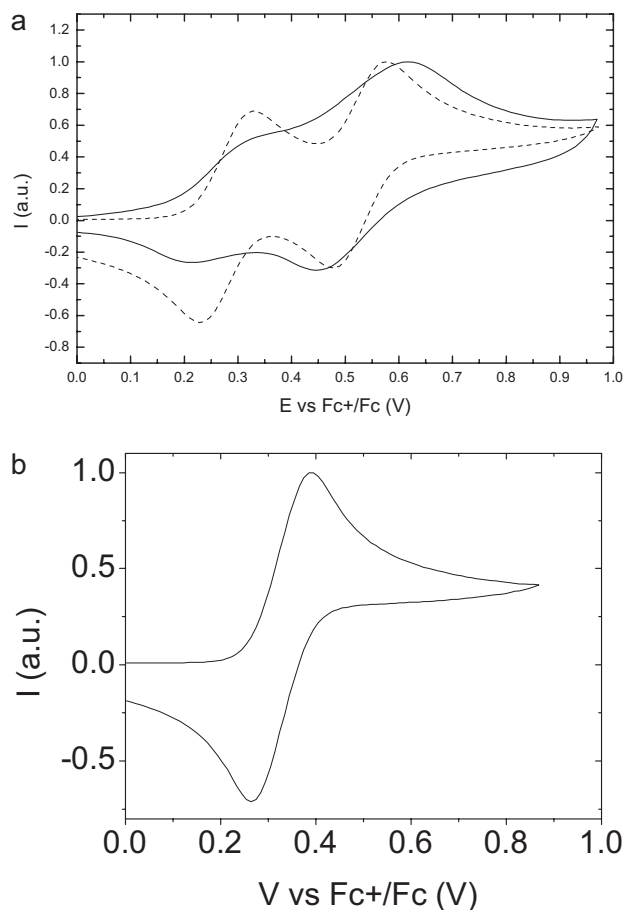


Figure 2. a) Cyclic voltammograms of TPD (dashed line) and pTPD (solid line). b) Cyclic voltammogram of tri-tolylamine.

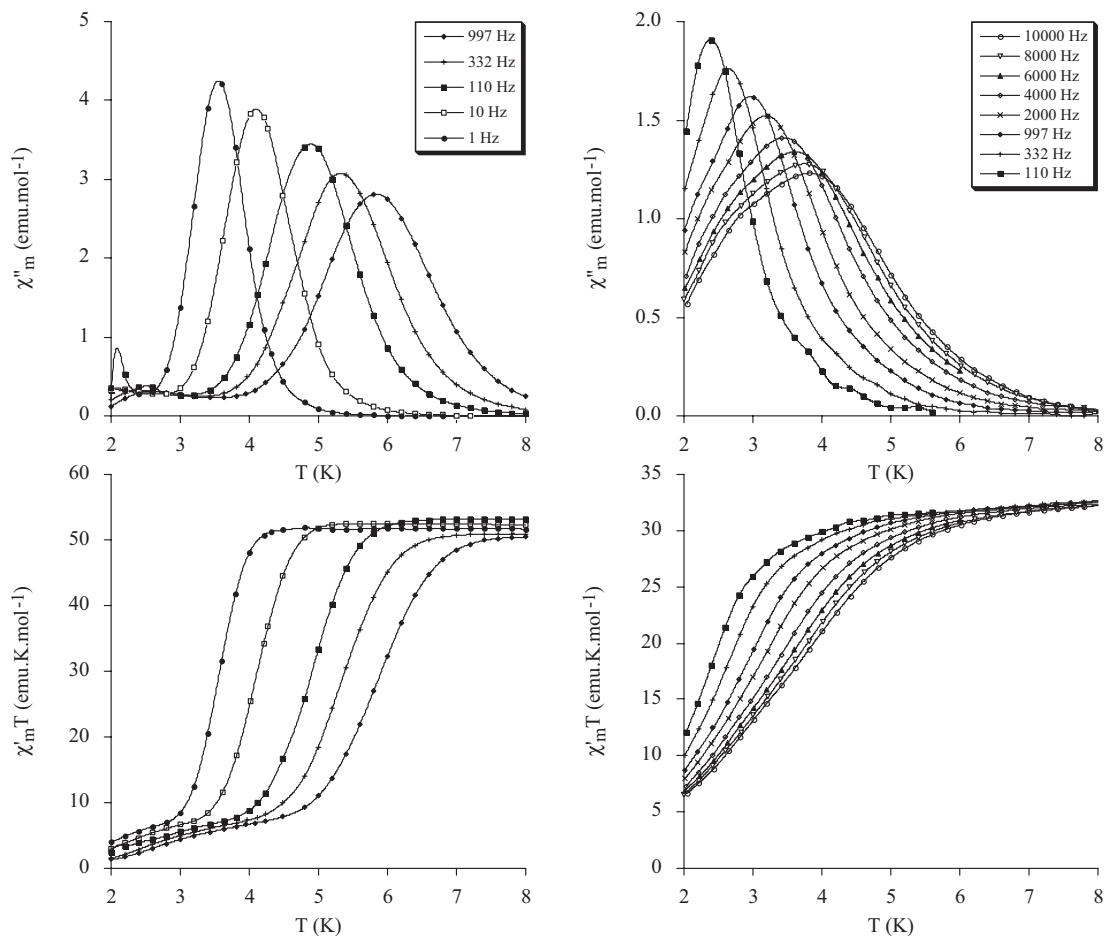


Figure 3. Plots of χ''_m versus T (top row) and $\chi'_m T$ versus T (bottom row) for a crystalline sample of $\text{Mn}_{12}\text{PhF}_5$ (left column) and for a pTPD/ $\text{Mn}_{12}\text{PhF}_5$ 8:2 film (right column) in a 3.95×10^{-4} T AC field oscillating at the indicated frequencies, where χ''_m and χ'_m are the out-of-phase and in-phase magnetic susceptibilities, respectively ($1 \text{ emu} = 10^{-3} \text{ A m}^2$).

These χ'' peaks appear at lower temperatures for the $\text{Mn}_{12}\text{PhF}_5$ /pTPD films than for the $\text{Mn}_{12}\text{PhF}_5$ crystals, indicating that the relaxation of the magnetization is faster in the films. For films with decreasing concentrations of $\text{Mn}_{12}\text{PhF}_5$, the magnetic response decreases in magnitude, but the χ'' behavior remains unchanged, indicating the molecular origin of this behavior. Analysis of the frequency (ν) dependence of the χ'' peaks through an Arrhenius plot permits estimation of the magnetization-relaxation parameters in these systems (Fig. 4).

These data fit to the equation $\tau = \tau_0 \exp(U_{\text{eff}}/k_B T)$, where τ is the relaxation time, U_{eff} is the effective potential-energy barrier that the molecular magnet has to overcome to flip its magnetic moment from spin “up” to spin “down” states, k_B is the Boltzmann constant, and T is the temperature. The effective energy barrier U_{eff} for the films was determined to be 28.6 K with a pre-exponential factor, τ_0 , of 9.8×10^{-9} s, while for the crystals these values are $U_{\text{eff}}/k_B = 62.3$ K and $\tau_0 = 4.0 \times 10^{-9}$ s. Hence, the U_{eff} value for the film was significantly lower than that found in the crystals. This low value is characteristic of the two-electron-reduced $[\text{Mn}_{12}\text{PhF}_5]^{2-}$ species. In fact, very few

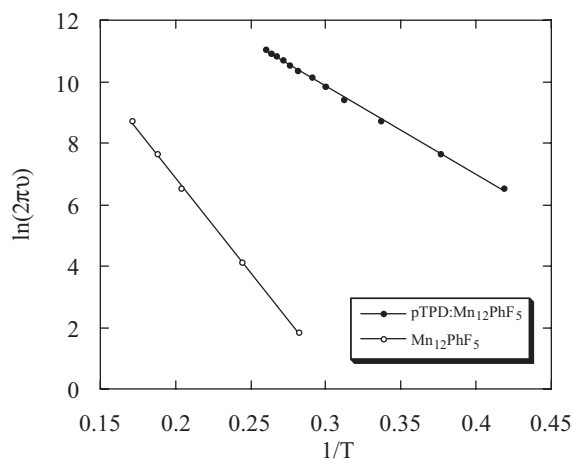


Figure 4. Plot of the natural logarithm of the inverse magnetization-relaxation rates ($\tau = 1/2\pi\nu$, where ν is the frequency of the oscillating field) versus the inverse of the absolute temperature for a pTPD/ $\text{Mn}_{12}\text{PhF}_5$ (8:2) film (closed circles) and for the $\text{Mn}_{12}\text{PhF}_5$ crystal (open circles). The solid lines represent least-square fits of the data to the Arrhenius equation.

examples of $[\text{Mn}_{12}]^{2-}$ species have been reported so far. In these anions, the U_{eff} values have been found to be clearly lower than those reported for $[\text{Mn}_{12}]^-$ and neutral Mn_{12} species (which are ca. 50 K and 60 K, respectively).^[18] From these data, one can conclude that in the pTPD films containing the $\text{Mn}_{12}\text{PhF}_5$ complex, the manganese clusters have been reduced by two electrons, and therefore the amount of oxidized pTPD units is twice the amount of $\text{Mn}_{12}\text{PhF}_5$ molecules embedded in the conducting polymer. It is to be noted that these magnetic properties unambiguously demonstrate that in the conductive film, $\text{Mn}_{12}\text{PhF}_5$ was exclusively present as reduced dianions. In fact, a comparison between the crystal and a film formed from pTPD containing 20 % of $\text{Mn}_{12}\text{PhF}_5$ (Fig. 3) shows that, in the crystal, a single χ'' peak is observed at ca. 5 K at a frequency of 110 Hz. This peak has to be taken as the signature of the neutral $\text{Mn}_{12}\text{PhF}_5$ molecule. In the conducting film, a single peak with similar width appeared at 2.5 K at the same frequency, while no peak was observed at 5 K.

It is important to notice that in the pTPD, the number of hopping sites is well-defined as they coincide with the hTPD sites. Therefore, when a known amount of $\text{Mn}_{12}\text{PhF}_5$ molecules is added to the pTPD, it is possible to determine the amount of oxidized pTPD units. As one $\text{Mn}_{12}\text{PhF}_5$ molecule is capable of oxidizing two hTPD moieties, the total number of free charges is twice the number of $\text{Mn}_{12}\text{PhF}_5$ molecules added, assuming the conductivity is solely occurring based on holes. If the electrons also participate in the conduction process via hopping between the reduced $\text{Mn}_{12}\text{PhF}_5$ anions, one can predict that each $\text{Mn}_{12}\text{PhF}_5$ gives rise to four free charges (resulting from two holes on the polyarylamine and two electrons on the $\text{Mn}_{12}\text{PhF}_5$ site). These features can facilitate the study of the charge-transport properties of these films as a function of the amount of oxidized hTPD units. When pTPD was oxidized with $\text{Mn}_{12}\text{PhF}_5$, the conductivity of the film increased significantly with the amount of oxidant (Fig. 5a). High conductivities on the order of 0.01 S cm^{-1} were obtained at ratios of $\text{Mn}_{12}\text{PhF}_5/\text{hTPD}$ above 0.02 ($\text{hTPD}^+/\text{hTPD} > 0.04$). These conductivities were sufficiently high so that this composite could be used as a charge-transporting material for OLEDs and organic solar cells.^[19] Both the high conductivities and the relatively low levels of oxidation needed to obtain them are surprising.

First, we would like to comment on the high conductivity levels reached in these films. These values are three orders-of-magnitude higher than those found in highly oxidized arylamine-based MDPs.^[11–13] They resemble those reported for thin films of chemically oxidized conjugated thiophene oligomers, despite the limited conjugation between adjacent TPD moieties compared to the conjugation existing in an oligothiophene.^[20] An effect that strongly influences the overall conductivity is the intersite hopping. For reasons not yet understood, the intersite hopping might be better in the pTPD chain than in oligothiophenes.

Second, and perhaps more surprising than the absolute values of the conductivities, is the low level of oxidized sites needed to reach these values. At $\text{Mn}_{12}\text{PhF}_5/\text{hTPD}$ ratios of

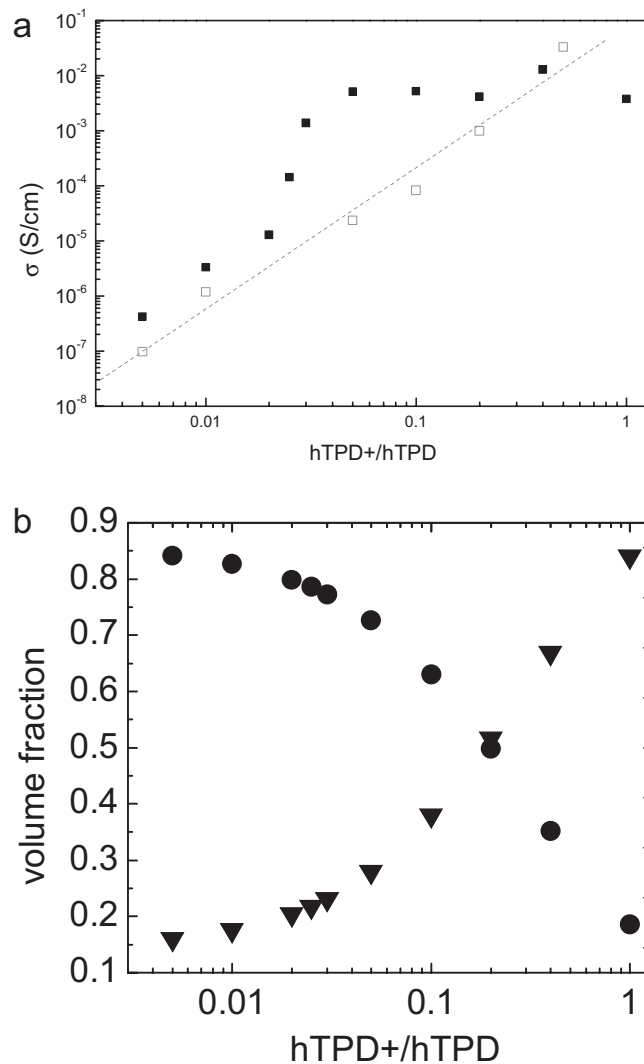


Figure 5. a) Conductivity of pTPD films as a function of the oxidized hTPD units using $\text{Mn}_{12}\text{PhF}_5$ as oxidant (■) and when using AgSbF_6 as oxidant (□); the dashed line is a linear fit for the AgSbF_6 -doped film. The $\text{hTPD}^+/\text{hTPD}$ ratio corresponds to two times the $\text{Mn}_{12}\text{PhF}_5/\text{hTPD}$ ratio when $\text{Mn}_{12}\text{PhF}_5$ is used as the oxidant. b) Volume fraction of $\text{Mn}_{12}\text{PhF}_5$ (▼) and TPD units (●) as a function of oxidized hTPD units.

around 0.02 ($\text{hTPD}^+/\text{hTPD} > 0.04$), which equals 2×10^{19} oxidized sites per cubic centimeter, the conductivity rapidly increased by two orders of magnitude, after which it remained relatively constant up to high doping ratios. In conjugated oligomers or polymers such as polythiophene, conductivities of 0.01 S cm^{-1} are reached at much higher concentrations of oxidized sites, ranging from 5×10^{20} to $1 \times 10^{21} \text{ cm}^{-3}$.^[21] This shows that the $\text{Mn}_{12}\text{PhF}_5/\text{pTPD}$ hybrid material shows superior conductivity, even with respect to oxidized conjugated polymers, at low levels of oxidation.

To verify if this rapid increase in conductivity at low oxidation levels occurs in pTPD polymers doped with classical oxidants, we have investigated the conductivities of pTPD films as a function of AgSbF_6 . As can be seen from the open squares

in Figure 5a, the conductivity increases linearly in the log–log presentation, and no sudden increase in conductivity is observed at low oxidation levels. This implies that the $\text{Mn}_{12}\text{PhF}_5$, apart from functioning as an oxidant for pTPD, plays an additional role in the transport properties of the pTPD/ $\text{Mn}_{12}\text{PhF}_5$ material. One possibility is that $\text{Mn}_{12}\text{PhF}_5$ contributes to the rise in conductivity via inter-cluster electron hopping. In fact, this hopping process has already been proposed to explain the semiconducting properties of crystals of Mn_{12} acetate.^[22] In our case, the rise in conductivity occurred at a $\text{Mn}_{12}\text{PhF}_5$ volume fraction of around 14 %, which is close to that needed to form a percolating network of $\text{Mn}_{12}\text{PhF}_5$ clusters.^[23] However, when studying the conductivities of a TPD/polystyrene MDP as a function of amount of $\text{Mn}_{12}\text{PhF}_5$, we found an increase in conductivity with increasing $\text{Mn}_{12}\text{PhF}_5$ levels, showing a linear increase on a log–log presentation reaching 10^{-6} Scm^{-1} for a $\text{Mn}_{12}\text{PhF}_5$ /TPD ratio of 0.2. This conductivity is much lower than observed in the $\text{Mn}_{12}\text{PhF}_5$ /pTPD films and thus rules out inter-cluster electron hopping as a reason for the high conductivities observed in these films. Hence, a synergic interaction between the $\text{Mn}_{12}\text{PhF}_5$ and the pTPD seems to be taking place in these films. The hole mobility through the TPD moieties is improved by the presence of the Mn_{12} anions, which seems to reduce the energy barrier for hopping due to electrostatic interactions. From temperature-dependent conductivity measurements, Arrhenius activation energies were obtained ranging from 0.3 eV to 0.2 eV from the low- to high-doping-level regime, respectively. No decrease in activation energy was observed at doping ratios where the conductivity of the hybrid films rose rapidly. In a future paper, a model describing this data will be presented.

A final point that needs explanation is the observation that the conductivity remained at a constant level over a wide range of $\text{Mn}_{12}\text{PhF}_5$ /hTPD ratios (0.02–0.5). This is also surprising, as generally conductivity is expected to decrease with increasing intersite TPD distances.^[24] Even though the conductivity is expected to increase with increasing amount of oxidized molecules, it is unexpected that the effect of more free carriers and larger intersite distances result in a constant conductivity. If we assume that the charge transport occurs solely through the pTPD network, it is difficult to understand that, for high volume fractions of $\text{Mn}_{12}\text{PhF}_5$ (as high as 80 %), which implies a high dilution of the pTPD chains, the conductivity does not decrease (Fig. 5b). This suggests that at high levels of doping $\text{Mn}_{12}\text{PhF}_5$ must also contribute to the charge-transport process.

In conclusion, we have prepared a soluble hybrid organic–inorganic semiconductor based on the synergy between an arylamine polymer and the molecular nanomagnet [$\text{Mn}_{12}\text{O}_{12}(\text{H}_2\text{O})_4(\text{C}_6\text{F}_5\text{COO})_{16}$]. At $\text{Mn}_{12}\text{PhF}_5$ /hTPD ratios as low as 0.02, the conductivity of the hybrid films reaches values around 0.01 Scm^{-1} . This high conductivity, in combination with the low amount of oxidized transport sites needed to obtain it, makes this material very suitable as a charge-transport material in organic solar cells and in organic light-emitting diodes.

In terms of magnetism research, this hybrid material constitutes the first attempt to embed a Mn_{12} nanomagnet into a conducting polymer. The presence of the semiconducting polymer does not seem to affect the magnetism, as expected for isolated molecules. However, the high conductivities observed in this hybrid material imply that the Mn_{12} clusters play an important, although as yet not completely understood, role in the electrical properties of these hybrid materials.

Experimental

Poly(*N,N'*-diphenyl-*N,N'*bis(4-hexylphenyl)-[1,1'-biphenyl]-4,4'-diamine) (pTPD) was obtained from American Dye Source and used without further purification. The solvents used were obtained from Aldrich. $\text{Mn}_{12}\text{PhF}_5$ was prepared using the ligand-substitution method [25]. Oxidation of the pTPD films was done in chlorobenzene solution by slowly adding a dilute solution of $\text{Mn}_{12}\text{PhF}_5$ in dichloromethane. In the case when AgSbF_6 was used as the oxidant, the resulting solution was centrifuged and decanted to remove the solid silver that resulted from the redox reaction. Finally, before spin-coating, the solutions were filtered over a $0.45 \mu\text{m}$ polytetrafluoroethylene filter. Films were spin-coated from a chlorobenzene/dichloromethane (3:1 v/v) solution onto quartz plates with photolithographically defined interdigitated Pt electrodes. The thickness of the films was determined using an Ambios XP1 profilometer. Electrical measurements were performed using a Keithley 2400 source meter. The current was found to be proportional to the voltage, and the resistivity was determined from the slope of the current–voltage curves. Temperature-dependent electrical measurements were performed on a Physical Property Measurement System (Quantum Design PPMS-9) equipped with a liquid-He Dewar, permitting a temperature range from 300 K to 2 K. Oxidation and reduction potentials were determined using an Autolab potentiostat, Pt working and counter electrodes, and a Ag/AgNO_3 reference electrode. Voltages are reported relative to the ferrocene/ferrocenium couple.

Received: September 13, 2004
Final version: January 24, 2005

- [1] E. Coronado, J. R. Galán-Mascarós, C. J. Gómez-García, V. Laukhin, *Nature* **2000**, *408*, 447.
- [2] P. Gomez-Romero, *Adv. Mater.* **2001**, *13*, 163.
- [3] *Functional Hybrid Materials* (Eds: P. Gómez-Romero, C. Sanchez), Wiley-VCH, Weinheim, Germany **2004**.
- [4] H. C. Stark GmbH, *BAYTRON Coating Guide*, Issue 10/2002, Goslar, Germany, **2002**.
- [5] For examples of polyaniline dispersions, see Ormecon International, <http://www.ormecon.de/> (accessed August, 2004).
- [6] P. M. Borsenberger, D. S. Weiss, *Organic Photoreceptors for Xerography*, Marcel Dekker, New York **1998**.
- [7] C. D. Muller, A. Falcou, N. Reckefuss, M. Rojahn, V. Wiederhirm, P. Rudati, H. Frohne, O. Nuyken, H. Becker, K. Meerholz, *Nature* **2003**, *421*, 829.
- [8] M. T. Bernius, M. Inbasekaran, J. O'Brien, W. S. Wu, *Adv. Mater.* **2000**, *12*, 1737.
- [9] C. Ganzorig, M. Fujihira, *Appl. Phys. Lett.* **2000**, *77*, 4211.
- [10] X. Zhou, M. Pfeiffer, J. Blochwitz, A. Werner, A. Nollau, T. Fritz, K. Leo, *Appl. Phys. Lett.* **2001**, *78*, 410.
- [11] J. Mort, S. Grammatica, D. J. Sandman, A. Troup, *J. Electron. Mater.* **1980**, *9*, 411.
- [12] A. Troup, J. Mort, S. Grammatica, D. J. Sandman, *J. Non-Cryst. Solids* **1980**, *35*, 151.
- [13] Y. Shen, K. Diest, M. H. Wong, B. R. Hsieh, D. H. Dunlap, G. Malliaras, *Phys. Rev. B: Condens. Matter Mater. Phys.* **2003**, *68*, 81 204.

- [14] V. G. Kytin, J. Bisquert, H. J. Bolink, unpublished.
- [15] a) R. Sessoli, D. Gatteschi, A. Caneschi, M. Novak, *Nature* **1993**, 365, 141. b) J. R. Friedman, M. P. Sarachick, J. Tejada, R. Ziolo, *Phys. Rev. Lett.* **1996**, 76, 3830. c) L. Thomas, F. Lionti, R. Ballou, D. Gatteschi, R. Sessoli, B. Barbara, *Nature* **1996**, 383, 145. d) B. Schwarzschild, *Phys. Today* **1997**, 50(1), 17. e) R. Sessoli, D. Gatteschi, *Angew. Chem. Int. Ed.* **2003**, 42, 268.
- [16] J. Tejada, E. M. Chudnovsky, E. Del Barco, J. M. Hernández, T. P. Spiller, *Preprint Archive, Condensed Matter* <http://arxiv.org/abs/cond-mat/0009432>.
- [17] M. Soler, S. K. Chandra, D. Ruiz, E. R. Davidson, D. N. Hendrickson, G. Christou, *Chem. Commun.* **2000**, 2417.
- [18] T. Kuroda-Sowa, M. Lam, A. L. Rheingold, C. Frommen, W. M. Reiff, M. Nakano, J. Yoo, A. L. Maniero, L. Brunel, G. Christou, D. N. Hendrickson, *Inorg. Chem.* **2001**, 40, 6469.
- [19] H. J. Bolink, M. Buechel, B. Jacobs, M. de Kok, M. Ligter, E. A. Meulenkaamp, S. Vulto, P. Van der Weijer, *Proc. SPIE-Int. Soc. Opt. Eng.* **2002**, 4800, 1.
- [20] D. M. de Leeuw, *Synth. Met.* **1993**, 55, 3597.
- [21] C. P. Jarret, R. H. Friend, A. R. Brown, D. M. de Leeuw, *J. Appl. Phys.* **1995**, 77, 6289.
- [22] J. M. North, D. Zipse, N. S. Dalal, E. S. Choi, E. Jobilong, J. S. Brooks, D. L. Eaton, *Phys. Rev. B: Condens. Matter Mater. Phys.* **2003**, 67, 174407.
- [23] H. Scher, R. Zallen, *J. Chem. Phys.* **1970**, 53, 3759.
- [24] a) H. Bassler, *Philos. Mag. B* **1984** 50, 347. b) H. Bassler, *Phys. Status Solidi B* **1993**, 175, 15.
- [25] H. J. Eppley, H. L. Tsai, N. D. Vries, K. Folting, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* **1995**, 117, 301.

Bacteriorhodopsin Monolayers for Optoelectronics: Orientation and Photoelectric Response on Solid Supports**

By Tao He, Noga Friedman, David Cahen,* and Mordechai Sheves*

Bacteriorhodopsin (bR) is an integral protein, with a supramolecular organization, found in the purple membrane (PM) of *Halobacterium salinarum*.^[1] Following light absorption, bR releases protons into the outer medium and takes up protons on the cytoplasmic (CP) side of the cell, accompanied by an

immediate charge-separation step and an energy gradient across the cell membrane.^[2-4] At the same time, bR undergoes a photochemical cycle, passing through a series of intermediate states, referred to as the J, K, L, M, N, and O states.^[5-7] The M state exhibits the strongest spectral shift (absorbing at 412 nm) and the highest population of all the intermediates under steady-state illumination, and it decays thermally or upon blue-light irradiation. Even more important is that the photosensitivity of this biological photochrome and the cyclivity of its response to illumination is far better than that of synthetic materials.^[7] In addition, bR exhibits long-term stability over a wide range of pH, temperature, and humidity values, and it does so in a variety of (photo)chemical environments.^[7] All of these properties make it a promising biomaterial for optical and photoelectric applications.^[2,6-9] From engineering considerations, however, PM fragments should be immobilized or assembled onto solid supports before the protein can be incorporated into functional devices. Furthermore, to generate a maximal photoelectric response for the whole system upon photon absorption, macroscopic orientation of the PM fragments is vital. This is due to the highly directional nature of this membrane protein, in which membrane orientation determines the polarity of the photoelectric response.^[9,10] Among the methods used so far for membrane immobilization, we note Langmuir-Blodgett (LB) deposition,^[11-14] electrostatic (layer-by-layer) self-assembly,^[8,15] molecular recognition,^[9,16] adsorption onto a lipid monolayer,^[17] and sedimentation under a direct-current (DC) bias^[18] or under the combined action of electric and magnetic fields.^[19] In addition to the orientation, the thickness of bR films should also be controlled for the fabrication of bR-based bio-optoelectronic devices, especially if the nanometer-sized dimensions of the membranes are to be exploited.

Constructing a monolayer of bR onto a solid support allows, in principle, the best possible control over film orientation and, thus, should yield the most reproducible results. We show here how to prepare such monolayers and present data indicating that a monolayer of native bR can be converted completely to the M intermediate under steady-state irradiation, even at 87% humidity and at pH 7. This is remarkable because in multilayers under similar conditions or in suspensions (pH 7), the M state does not accumulate.

bR monolayers were prepared by a self-assembly procedure. Atomic force microscopy (AFM) topography, ellipsometry, UV-vis absorption spectroscopy, and Fourier-transform infrared (FTIR) absorption spectroscopy indicated the presence of a reasonably dense net of PM patches on the solid surface. Both the AFM images (Fig. 1) and the ellipsometric data indicated that the resulting thin film was a monolayer with partially overlapping patches. The size of the PM patches ranged from several hundreds of nanometers to several micrometers, and their thicknesses were about 5–6 nm, in agreement with values in the literature.^[7] The coverage increased on increasing the concentration of the PM suspensions. However at high coverage, the fraction of partially overlapping PM patches increased, i.e., a multilayer started to form on the

[*] Prof. D. Cahen, Dr. T. He
Department of Materials and Interfaces
Weizmann Institute of Science
Rehovot 76100 (Israel)
E-mail: david.cahen@weizmann.ac.il
Prof. M. Sheves, Dr. N. Friedman
Department of Organic Chemistry
Weizmann Institute of Science
Rehovot 76100 (Israel)
E-mail: mudi.sheves@weizmann.ac.il

[**] We thank the Israel Ministry of Science for support (strategic research Tashtyoth). T. H. thanks J. Ghabboun, S. Rühle, A. Salomon, I. Visoly-Fisher for help in experiments, and the Clore foundation for a postdoctoral fellowship.