NMR Spectroscopy

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Improved Dynamic Nuclear Polarization Surface-Enhanced NMR Spectroscopy through Controlled Incorporation of Deuterated Functional Groups**

Alexandre Zagdoun, Aaron J. Rossini, Matthew P. Conley, Wolfram R. Grüning, Martin Schwarzwälder, Moreno Lelli, W. Trent Franks, Hartmut Oschkinat, Christophe Copéret, Lyndon Emsley, and Anne Lesage**

High-field dynamic nuclear polarization (DNP) is emerging as an extremely powerful method to enhance the NMR sensitivity of solid samples.[1–3] By transferring polarization from unpaired electrons (usually from stable exogenous radicals that are introduced by impregnating or dissolving the sample with a radical-containing solution) to nuclei, DNP has the potential to yield signal enhancements of several orders of magnitude. DNP has been successfully applied to the investigation of various biological samples.[4–7] In parallel, the potential of high-field solid-state DNP has been demonstrated for materials science,[8–12] or most recently to enhance the NMR sensitivity of bulk microcrystalline solids.[13]

However, even with DNP, the overall NMR sensitivity is still the limiting factor in many applications, and developing improved DNP conditions is thus of primary importance in this field. Many parameters are known to influence the efficiency of the electron–nucleus, and of the subsequent internuclear, polarization transfer. For instance, the structure and properties of the exogenous polarizing radical have been shown to dramatically impact the DNP enhancements.[11,14–16] The temperature of the sample, the spinning frequency and/or the properties of the solvent itself are other key factors that influence the DNP efficiency.[17–21]

In these experiments, polarization follows a complex trajectory from the electron to the target NMR nucleus. Electron polarization is transferred to the protons by saturating the electron spin. The resulting enhanced nuclear polarization is then propagated through the sample by spin-diffusion-like mechanisms,[22–24] and cross-polarization (CP) is usually applied to transfer polarization from the hyperpolarized protons to lower-gamma nuclei. In this process, the proton longitudinal relaxation time ($T_1(^1H)$) plays a key role. In particular, it was recognized early on that $T_1(^1H)$ usually defines the polarization build-up rate, and that in cases where $T_1(^1H)$ is short, the enhanced polarization is rapidly dissipated through relaxation, before it can be accumulated and distributed throughout the sample.[25] The DNP efficiency is thus expected to diminish with short proton T_1. It was shown for instance that, when using nanodiamonds as the polarization source, DNP efficiency decreases with the $T_1(^1H)$.[26] On the other hand, as $T_1(^1H)$ governs the polarization build-up rates, and thus the interscan delays, it has been shown that a gain in sensitivity per unit time can be attained with short T_1.[17,20,27,28]

Herein, we show that when a substrate possesses methyl groups that have short T_1 values, these protons act as relaxation sinks and dramatically reduce DNP enhancements. We then illustrate how the DNP enhancement can be restored by replacing these fast-relaxing protons with deuterons, or with functional groups that contain slowly relaxing protons. Furthermore, we show that, for DNP surface-enhanced NMR experiments, in particular, the size and polarity of these groups have a considerable impact on the overall NMR sensitivity; they affect the number of detectable nuclear spins in the sample and the NMR relaxation parameters, because bulky apolar surface functional group repel the polarizing radicals from the surface. By replacing methyl groups with deuterated analogues, the overall sensitivity enhancements (Σ)[27] can go from 12 to 55.

The studies here were performed in the context of DNP surface-enhanced NMR spectroscopy (SENS)[8] with a series of mesostructured hybrid organosilica materials that contain surface propylazide fragments. These samples were obtained by condensing tetraethoxyorthosilicate and 3-azidopropyltrimethoxy silane in the presence of a structure-directing agent (P123).[11,29–31] The resulting material (**Mat-PrN$_3$**, Figure 1 A) contains roughly five terminating surface silanols per propy-

[*] A. Zagdoun, Dr. A. J. Rossini, Dr. M. Lelli, Prof. Dr. L. Emsley, Dr. A. Lesage
Centre de RMN à Très Hauts Champs
Université de Lyon (CNRS/ENS/UCB Lyon 1)
5 rue de la Doua 69100 Villeurbanne (France)
E-mail: lyndon.emsley@ens-lyon.fr
anne.lesage@ens-lyon.fr
Homepage: http://crmn.ens-lyon.fr
Dr. M. P. Conley, W. R. Grüning, M. Schwarzwälder, Prof. Dr. C. Copéret
Department of Chemistry, ETH Zürich
Laboratory of Inorganic Chemistry
Wolfgang Pauli Strasse 10, 8093 Zürich (Switzerland)
Dr. W. T. Franks, Prof. Dr. H. Oschkinat
FMP, Leibniz-Institut für Molekulare Pharmakologie
Robert-Rössle-Str. 10, 13125 Berlin (Germany)

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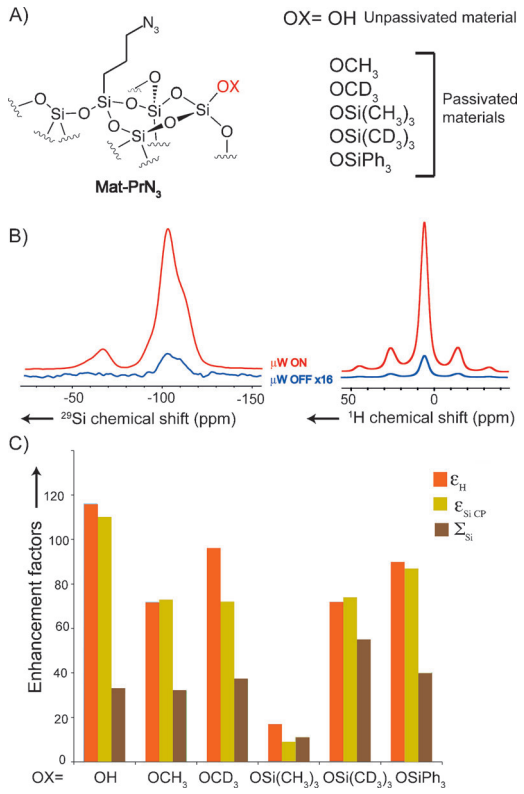

Figure 1. A) Molecular structure of the materials investigated during this study. B) ^{1}H echo (right) and ^{29}Si CP MAS spectra (left) of unpassivated Mat-PrN$_3$ impregnated with a 16 mM bCTbK solution in tetrachloroethane, acquired with (red) and without (blue) microwave irradiation. C) Proton enhancement (ε_H), silicon enhancement ($\varepsilon_{Si\,CP}$) and overall sensitivity enhancement (Σ) as a function of the passivating groups. All experiments were recorded at 400 MHz (proton frequency) with a spinning frequency of 8 kHz. A detailed description of Σ is given in the Supporting Information.

lazide unit. Functionalization of these remaining silanols is often desired to tune the hydrophobicity and reactivity of the silica surface.[32–34] In particular, OSiMe$_3$ (TMS) fragments are usually incorporated during the stepwise synthesis of catalytic materials.[35,36] Note that TMS here refers to the OSiMe$_3$ surface group and should not be mistaken with tetramethylsilane, a molecule often used as a reference in NMR spectroscopy. Coating the silica surface with unreactive TMS fragments allows for the subsequent selective grafting of active metal complexes. Other passivating agents can also be used (Figure 1), thus making this material an ideal scaffold for relating the properties of the surface groups to the DNP efficiency.

The synthesis of the materials containing TMS, perdeuterated TMS ([D$_9$]-TMS), methoxy, deuterated methoxy ([D$_3$]-methoxy), and OSiPh$_3$ (TPS) passivating groups is described in the Supporting Information. A 16 mM solution of bCTbK in 1,1,2,2-tetrachloroethane was used as a polarizing mixture. This combination of solvent and biradical has previously given high DNP enhancements (ε) of approximately 100 on unpassivated **Mat-PrN$_3$**.[11] All experiments were carried out at a temperature of approximately 100 K on a commercial Bruker 400 MHz DNP spectrometer.[20] Figure 1 C shows the proton (ε_H solvent) and silicon ($\varepsilon_{Si\,CP}$) signal enhancement factors for the different samples. The overall sensitivity enhancement (Σ),[28] which takes into account both the loss of the NMR signal owing to the introduction of a paramagnetic radical (i.e. the quenching or bleaching effects)[27,28,37] and the subsequent changes in T_1(^{1}H), is also shown. Table 1 gives the T_1(^{1}H) of the solvent and the surface protons involved in CP.

Table 1: Proton longitudinal relaxation times, silicon-29 enhancements, and overall sensitivity enhancements of **Mat-PrN$_3$** with various passivating surface groups.

	OH	OCH$_3$	OCD$_3$	TMS	[D$_9$]-TMS	OSiPh$_3$
T_1(^{1}H) [s][a]	3.03(3)	3.03(4)	3.59(4)	1.0(1)	2.81(2)	3.06(4)
T_1(^{1}H)$_{29Si}$ [s][b]	2.40(2)	2.23(1)	2.67(2)	0.89(2)	3.15(3)	2.7(1)
$\varepsilon_{Si\,CP}$[c]	110(3)	71(3)	72(3)	9(3)	74(3)	87(3)
Σ_{Si}[d]	33	31	38	11	55	40

[a] Proton longitudinal relaxation times measured by direct acquisition and [b] by ^{29}Si CP (see the Supporting Information for experimental details). [c] ^{29}Si enhancement measured by ^{1}H CP and, [d] overall ^{29}Si sensitivity enhancement.

In most cases ε_H and $\varepsilon_{Si\,CP}$ match within error, as do the T_1(^{1}H) for the bulk solvent and the surface ^{1}H nuclei. Carbon enhancements ($\varepsilon_{C\,CP}$) of the surface functional groups have also been measured and match ε_H and $\varepsilon_{Si\,CP}$ (see the Supporting Information). These observations are consistent with the solvent and surface protons existing within a single dipolar coupled proton spin bath where polarization is evenly distributed throughout the samples by proton–proton spin-diffusion mechanisms.[13,38]

An ε_H of 116 was obtained for the unpassivated **Mat-PrN$_3$** material; this result is consistent with the values obtained in previous studies on similar materials.[11] Upon replacement of the hydroxy group with TMS groups, ε_H is decreased to 17, which correlates with a sharp decrease of the proton T_1 from 3 s (in the presence of hydroxy groups) to 1 s. Such short T_1(^{1}H) values are expected in the presence of a high concentration of fast-rotating methyl groups at the temperature of the experiment here, that is, around 100 K. At significantly lower temperatures, tunneling mechanisms are expected to impact T_1.[39]

Next we investigated the effect of the selective deuteration of these surface methyl groups on T_1(^{1}H) and the DNP enhancements. Deuteration has long been used to optimize DNP enhancements. Deuteration of the solvent is widely used, and was proposed to lead to larger DNP enhancements owing to a decrease in the size of the proton bath and an increase in T_1(^{1}H).[21] Partial deuteration of exchangeable sites in an otherwise fully deuterated protein was also shown to improve enhancements by the same mechanism.[4,18] In both cases, the T_1(^{1}H) was only seen to significantly change at high deuteration levels.

When protonated TMS is replaced by [D$_9$]-TMS, T_1(^{1}H) increases to 3 s and consequently $\varepsilon_{Si\,CP}$ rises from 9 to 73. Less-pronounced effects were observed when the surface was passivated with methoxy and [D$_3$]-methoxy groups (Figure 1 c). T_1(^{1}H) did not substantially increase when the

methoxy groups were deuterated. Consistent with this observation no major difference in $\varepsilon_{Si\ CP}$ was observed. Methoxy groups likely have a smaller influence on $T_1(^1H)$ and $\varepsilon_{Si\ CP}$ than TMS groups owing to their lower proton densities.

The drastic increase of ε upon deuteration of TMS groups is clearly attributable to changes in the relaxation properties of the sample, rather than changes in the size of the proton spin bath, as is the case when using partially deuterated solvent.[18] Indeed, when the TMS groups were replaced by protonated TPS the enhancement was restored (Figure 1C). Materials passivated with TMS and TPS both have a similar overall proton density, with the primary difference being the longer $T_1(^1H)$ for the TPS passivated material (proton density is only affected very locally by the use of different passivating groups).

The detrimental impact of surface methyl groups on ε at 100 K was also confirmed by DNP NMR experiments conducted on a material containing imidazolium mesityl moieties (**Mat-Im**, structure shown in the Supporting Information) in place of the propylazide groups. **Mat-Im** materials contain three methyl groups on a mesityl ring in the organic fragment. For unpassivated **Mat-Im**, the ε_H and surface $T_1(^1H)$ were 40 and 1.7 s, respectively, as compared to 116 and 2.5 s for the unpassivated **Mat-PrN$_3$** material. Note that, as the electron relaxation time (T_{1e}) has been reported to be an important parameter for DNP,[11] T_{1e} was measured for all the passivated samples and no significant change was observed between samples (see the Supporting Information).

The above results clearly show that the presence of methyl groups, acting as relaxation sinks, directly impacts ε. If we now turn our attention to the overall NMR sensitivity enhancement Σ,[27] we note that the ratio Σ/ε is significantly higher for both TMS and [D$_9$]-TMS than for the other passivating groups. This finding is related to the fact that the decrease in the NMR signals as a result of paramagnetic effects is less pronounced in the presence of these passivating groups. This in turn suggests that these bulky groups prevent the close approach of the paramagnetic polarizing agents and the surface. Figure 2 shows the silicon-29 rotating-frame relaxation times $T_{1\rho}(^{29}Si)$ and the effective transverse dephasing times $T_2'(^{29}Si)$ as a function of the measured silicon-29 quenching factor θ_{Si} (the apparent fraction of nuclei contributing to the signal).[27] Both the relaxation times and θ_{Si} are expected to diminish when the surface and the radical are in close proximity. For materials passivated with TMS and [D$_9$]-TMS groups, θ_{Si} is high (>0.6) and both $T_{1\rho}(^{29}Si)$ and $T_2'(^{29}Si)$ are relatively long (>30 ms). Conversely, all other passivating groups lead to strong quenching effects (with θ_{Si} values between 0.2 and 0.4, that is, similar to values previously observed for mesoporous materials)[11,27] and short silicon relaxation times (between 11 and 20 ms). A strong correlation is observed between θ_{Si} and the two relaxation times, thus indicating that the short $T_{1\rho}$ and T_2' values observed for passivating groups other than TMS are due to proximity between the surface and the radical. We note that a doubling in θ_{Si} leads to a factor 2 gain in overall sensitivity. Finally, $T_2'(^{29}Si)$ was measured for the differently passivated **Mat-PrN$_3$** samples wetted with pure solvent (i.e., no biradical). In all cases, $T_2'(^{29}Si)$ was longer than 200 ms, thus confirming that

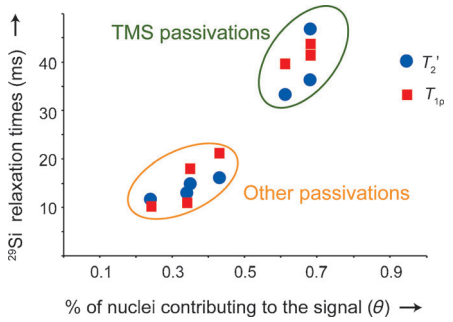

Figure 2. Silicon-29 rotating-frame relaxation times ($T_{1\rho}(^{29}Si)$) and effective transverse dephasing times ($T_2'(^{29}Si)$) plotted as a function of the quenching factor (θ_{Si}) for the various materials in a 16 mM solution of bCTbK in tetrachloroethane solution. A detailed description of θ_{Si} is given in the Supporting Information. $T_{1\rho}(^{29}Si)$ was measured with a 26 kHz spin-lock radio-frequency field. The individual values for each passivating group are given in the Supporting Information (Table S2 and Figure S3).

the differences observed in the silicon relaxation times are indeed due to paramagnetic effects rather than to the nature of the individual passivating groups (see the Supporting Information).

The shortening of these relaxation times is detrimental to many NMR experiments; with a short $T_{1\rho}$ CP will be less efficient, and a short T_2' will reduce the efficiency of any experiment containing a spin-echo block. A simple solution to increase T_2' would be to lower the radical concentration. However, as ε and Σ are highly dependent on the radical concentration, reducing the radical concentration would also diminish sensitivity enhancements. For challenging NMR experiments, in which sensitivity is an issue, both high enhancements and long transverse relaxation times are required. In many cases, lowering the radical concentration to obtain a T_2' that is long enough for these NMR experiments would lower the enhancements to the extent that sensitivity would be too low to perform such experiments. Passivation of the surface with bulky apolar groups, such as TMS, is a way to obtain high enhancements, lessen signal quenching by the radical, and maintain long T_2 values.

In summary, we have illustrated that surface groups that contain fast-relaxing protons act as polarization sinks in DNP SENS experiments of mesoporous hybrid materials, thus leading to a dramatic reduction in NMR sensitivity. By replacing these groups with deuterated analogues or with fragments that contain slowly relaxing protons, high sensitivity enhancement factors can be retrieved. Passivation of the surface with deuterated bulky apolar groups provides an additional increase in overall sensitivity, as they push the biradical away from the surface, thus leading to a reduction of the detrimental paramagnetic effects. The controlled incorporation of deuterated TMS increased Σ from 35 to 55 with respect to the starting unpassivated material, and from 12 to 55 for the material passivated with protonated TMS. This corresponds to a $\Sigma^{\dagger}$ (including Boltzmann factor) of 165, which leads to a reduction in experimental time of over four orders of magnitude with respect to ordinary room temperature solid-state NMR experiments. This result marks a sig-

nificant step forward in the context of the characterization of low surface area materials, including active heterogeneous catalysts, as these materials often contain surface functional groups containing methyl groups. These findings might also have potential implications in the field of protein sample preparation for DNP. Our study is in line with the observation of higher enhancements observed recently for deuterated proteins,[4,18] hinting at a dominant role of deuteration of those amino acids that contain fast-relaxing methyl groups. Finally, we note that solvents and supports (such as artificial membranes for oriented samples) containing methyl groups should not be used in DNP experiments.

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[1] L. Becerra, G. Gerfen, R. Temkin, D. Singel, R. Griffin, *Phys. Rev. Lett.* **1993**, *71*, 3561 – 3564.
[2] G. Gerfen, L. Becerra, D. Hall, R. Griffin, *J. Chem. Phys.* **1995**, *102*, 9494 – 9496.
[3] T. Maly, G. T. Debelouchina, V. S. Bajaj, K.-N. Hu, C.-G. Joo, M. L. Mak Jurkauskas, J. R. Sirigiri, P. C. A. van der Wel, J. Herzfeld, R. J. Temkin, et al., *J. Chem. Phys.* **2008**, *128*, 052211.
[4] T. Maly, D. Cui, R. G. Griffin, A.-F. Miller, *J. Phys. Chem. B* **2012**, *116*, 7055 – 7065.
[5] I. V. Sergeyev, L. A. Day, A. Goldbourt, A. E. McDermott, *J. Am. Chem. Soc.* **2011**, *133*, 20208 – 20217.
[6] A. H. Linden, S. Lange, W. T. Franks, Ü. Akbey, E. Specker, B.-J. van Rossum, H. Oschkinat, *J. Am. Chem. Soc.* **2011**, *133*, 19266 – 19269.
[7] M. Renault, S. Pawsey, M. P. Bos, E. J. Koers, D. Nand, R. Tommassen-van Boxtel, M. Rosay, J. Tommassen, W. E. Maas, M. Baldus, *Angew. Chem.* **2012**, *124*, 3053 – 3056; *Angew. Chem. Int. Ed.* **2012**, *51*, 2998 – 3001.
[8] A. Lesage, M. Lelli, D. Gajan, M. A. Caporini, V. Vitzthum, P. Miéville, J. Alauzun, A. Roussey, C. Thieuleux, A. Mehdi, et al., *J. Am. Chem. Soc.* **2010**, *132*, 15459 – 15461.
[9] M. Lelli, D. Gajan, A. Lesage, M. A. Caporini, V. Vitzthum, P. Miéville, F. Héroguel, F. Rascón, A. Roussey, C. Thieuleux, et al., *J. Am. Chem. Soc.* **2011**, *133*, 2104 – 2107.
[10] O. Lafon, M. Rosay, F. Aussenac, X. Lu, J. Trébosc, O. Cristini, C. Kinowski, N. Touati, H. Vezin, J.-P. Amoureux, *Angew. Chem.* **2011**, *123*, 8517 – 8520; *Angew. Chem. Int. Ed.* **2011**, *50*, 8367 – 8370.
[11] A. Zagdoun, G. Casano, O. Ouari, G. Lapadula, A. J. Rossini, M. Lelli, M. Baffert, D. Gajan, L. Veyre, W. E. Maas, et al., *J. Am. Chem. Soc.* **2012**, *134*, 2284 – 2291.
[12] A. J. Rossini, A. Zagdoun, M. Lelli, J. Canivet, S. Aguado, O. Ouari, P. Tordo, M. Rosay, W. E. Maas, C. Copéret, et al., *Angew. Chem.* **2012**, *124*, 127 – 131; *Angew. Chem. Int. Ed.* **2012**, *51*, 123 – 127.
[13] A. J. Rossini, A. Zagdoun, F. Hegner, M. Schwarzwälder, D. Gajan, C. Copéret, A. Lesage, L. Emsley, *J. Am. Chem. Soc.* **2012**, *134*, 16899 – 16908.
[14] K.-N. Hu, *Solid State Nucl. Magn. Reson.* **2011**, *40*, 31 – 41.
[15] C. Ysacco, H. Karoui, G. Casano, F. Moigne, S. Combes, A. Rockenbauer, M. Rosay, W. Maas, O. Ouari, P. Tordo, *Appl. Magn. Reson.* **2012**, *43*, 251 – 261.
[16] M. K. Kiesewetter, B. Corzilius, A. A. Smith, R. G. Griffin, T. M. Swager, *J. Am. Chem. Soc.* **2012**, *134*, 4537 – 4540.
[17] K. R. Thurber, W.-M. Yau, R. Tycko, *J. Magn. Reson.* **2010**, *204*, 303 – 313.
[18] Ü. Akbey, W. T. Franks, A. Linden, S. Lange, R. G. Griffin, B.-J. van Rossum, H. Oschkinat, *Angew. Chem.* **2010**, *122*, 7971 – 7974; *Angew. Chem. Int. Ed.* **2010**, *49*, 7803 – 7806.
[19] A. Zagdoun, A. J. Rossini, D. Gajan, A. Bourdolle, O. Ouari, M. Rosay, W. E. Maas, P. Tordo, M. Lelli, L. Emsley, A. Lesage, C. Copéret, *Chem. Commun.* **2012**, *48*, 654 – 656.
[20] M. Rosay, L. Tometich, S. Pawsey, R. Bader, R. Schauwecker, M. Blank, P. M. Borchard, S. R. Cauffman, K. L. Felch, R. T. Weber, R. J. Temkin, R. G. Griffin, W. E. Maas, *Phys. Chem. Chem. Phys.* **2010**, *12*, 5850.
[21] M. Rosay, PhD thesis, Massachuchetts Institute of Technology, **2001**.
[22] Y. Hovav, A. Feintuch, S. Vega, *J. Magn. Reson.* **2012**, *214*, 29 – 41.
[23] K. R. Thurber, R. Tycko, *J. Chem. Phys.* **2012**, *137*, 084508.
[24] A. Karabanov, I. Kuprov, G. T. P. Charnock, A. van der Drift, L. J. Edwards, W. Köckenberger, *J. Chem. Phys.* **2011**, *135*, 084106.
[25] A. Abragam, *Principles of Nuclear Magnetism*, Oxford University Press, Oxford, **1961**.
[26] L. B. Casabianca, A. I. Shames, A. M. Panich, O. Shenderova, L. Frydman, *J. Phys. Chem. C* **2011**, *115*, 19041 – 19048.
[27] A. J. Rossini, A. Zagdoun, M. Lelli, D. Gajan, F. Rascón, M. Rosay, W. E. Maas, C. Copéret, A. Lesage, L. Emsley, *Chem. Sci.* **2012**, *3*, 108 – 115.
[28] S. Lange, A. H. Linden, Ü. Akbey, W. T. Franks, N. M. Loening, B.-J. van Rossum, H. Oschkinat, *J. Magn. Reson.* **2012**, *216*, 209 – 212.
[29] F. Hoffmann, M. Cornelius, J. Morell, M. Fröba, *Angew. Chem.* **2006**, *118*, 3290 – 3328; *Angew. Chem. Int. Ed.* **2006**, *45*, 3216 – 3251.
[30] J. Nakazawa, T. D. P. Stack, *J. Am. Chem. Soc.* **2008**, *130*, 14360 – 14361.
[31] J. Nakazawa, B. J. Smith, T. D. P. Stack, *J. Am. Chem. Soc.* **2012**, *134*, 2750 – 2759.
[32] R. Anwander, I. Nagl, M. Widenmeyer, G. Engelhardt, O. Groeger, C. Palm, T. Röser, *J. Phys. Chem. B* **2000**, *104*, 3532 – 3544.
[33] J.-W. Park, Y. J. Park, C.-H. Jun, *Chem. Commun.* **2011**, *47*, 4860.
[34] K. Hara, S. Akahane, J. W. Wiench, B. R. Burgin, N. Ishito, V. S. Y. Lin, A. Fukuoka, M. Pruski, *J. Phys. Chem. C* **2012**, *116*, 7083 – 7090.
[35] T. K. Maishal, J. Alauzun, J.-M. Basset, C. Copéret, R. J. P. Corriu, E. Jeanneau, A. Mehdi, C. Reyé, L. Veyre, C. Thieuleux, *Angew. Chem.* **2008**, *120*, 8782 – 8784; *Angew. Chem. Int. Ed.* **2008**, *47*, 8654 – 8656.
[36] M. Baffert, T. K. Maishal, L. Mathey, C. Copéret, C. Thieuleux, *ChemSusChem* **2011**, *4*, 1762 – 1765.
[37] V. Vitzthum, F. Borcard, S. Jannin, M. Morin, P. Miéville, M. A. Caporini, A. Sienkiewicz, S. Gerber-Lemaire, G. Bodenhausen, *ChemPhysChem* **2011**, *12*, 2929 – 2932.
[38] Y. Hovav, A. Feintuch, S. Vega, *J. Chem. Phys.* **2011**, *134*, 074509.
[39] P. S. Allen, S. Clough, *Phys. Rev. Lett.* **1969**, *22*, 1351 – 1353.

