

The manuscript entitled "Dipolar Order Mediated  $^1\text{H} \rightarrow ^{13}\text{C}$  Cross-Polarization for Dissolution-Dynamic Nuclear Polarization" by Stuart J. Elliott et al. entails a discussion of an alternative way, apart from the Hartmann-Hahn cross-polarization method, to harness the high nuclear polarization of hyperpolarized  $^1\text{H}$  spins and transfer it to  $^{13}\text{C}$  spins via simpler, low-power and non-synchronized  $^1\text{H}$  and  $^{13}\text{C}$  *rf*-pulses.

In my opinion, the experimental demonstration of  $^1\text{H}$  to  $^{13}\text{C}$  polarization transfer mediated by dipolar order is certainly a welcome addition to the technical developments in (dissolution-dynamic nuclear polarization *d*DNP), in pursuit of simpler alternative to DNP cross polarization in terms of *rf*-hardware and *rf*-pulses. One of the main advantages of this reported technique is the use of non-simultaneous  $^1\text{H}$  and  $^{13}\text{C}$  *rf*-pulses in the DNP polarization transfer. This reported technique also opens up an avenue for polarizing larger DNP sample volumes with minimal probe arcing. For these and other reasons, I believe that this manuscript is significant in terms of scientific content and it brings some new technical insights to the magnetic resonance community, in particular to the rapidly growing *d*DNP field. Therefore, I would like to recommend publication of this manuscript with minor revision addressing the following suggestions and comments:

The author response is given in italics.

(Q1) Page 1: In the title, should it be "Dipolar Order-Mediated..." with the dash? (Q2) Page 1: lines 37 and 43—please spell out "typ." to typically. (Q3) Page 4: line 26—same comment as #2. (Q4) page 4: line 29—should be "the microwave is deactivated" (Q5) Page 7: Figure 4 caption, line 17—"nuclear Larmor frequency" was used twice; I suggest to use symbol omega or make it concise.

*(A1) The authors have changed the title. (A2,A3) These changes have been made throughout the manuscript. (A4) The spelling has been corrected. (A5) The authors will stick to the current notation in order to be consistent throughout the manuscript.*

(Q6) The authors mentioned that this dipolar order-mediated CP technique (~8.7%) is only about a half as efficient compared to the conventional CP-DNP technique (~20.4%) in terms of the final  $^{13}\text{C}$  DNP-enhanced polarization obtained. Do the authors have a  $^{13}\text{C}$  polarization value for direct  $^{13}\text{C}$  polarization (without CP or dipolar order CP) of this sample?

*(A6) The  $^{13}\text{C}$  nuclear polarization level for direct DNP was unfortunately not recorded for this sample because it is inefficient and displays a very long build-up time.*

(Q7) I assume these numbers (~8.7% for dipolar-order CP, ~20.4% for conventional CP) are solid-state  $^{13}\text{C}$  polarizations. Do the authors have liquid-state  $^{13}\text{C}$  polarization numbers (post dissolution)? These are not a requirement for this paper, but I think it would be good to report them if the data are available.

*(A7) The  $^{13}\text{C}$  nuclear polarization values presented were measured in the solid-state. Liquid state  $^{13}\text{C}$  polarization levels (post dissolution) could be measured in the future and be presented as part of a separate publication.*

(Q8) Obviously there's a lot of optimization to be done here in this preliminary technical report especially with DNP sample optimization. Can the authors expand on the possible effects of the efficiency of dipolar order-mediated CP if the  $^1\text{H}$  spin density is increased or decreased in the glassing matrix?

*(A8) Upon increasing the  $^1\text{H}$  spin density within the glassing matrix, an improvement is observed in the performance of the *d*CP *rf*-pulse sequence with respect to that of a sophisticated and high *rf*-power CP experiment.*