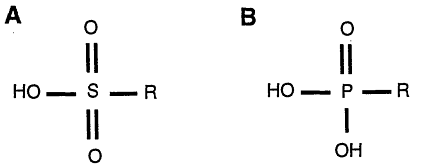
Sulfur and Hydrogen Isotope Anomalies in Meteorite Sulfonic Acids

George W. Cooper,* Mark H. Thiemens, Teresa L. Jackson, Sherwood Chang

Intramolecular carbon, hydrogen, and sulfur isotope ratios were measured on a homologous series of organic sulfonic acids discovered in the Murchison meteorite. Mass-independent sulfur isotope fractionations were observed along with high deuterium/hydrogen ratios. The deuterium enrichments indicate formation of the hydrocarbon portion of these compounds in a low-temperature environment that is consistent with that of interstellar clouds. Sulfur-33 enrichments observed in methanesulfonic acid could have resulted from gas-phase ultraviolet irradiation of a precursor, carbon disulfide. The source of the sulfonic acid precursors may have been the reactive interstellar molecule carbon monosulfide.

Previous isotopic measurements of organic compounds from the Murchison meteorite, a carbonaceous chondrite, have shown that water-soluble polar organic compounds generally have high $^{2}H/H$ (D/H), $^{13}C/^{12}C$, and $^{15}N/^{14}N$ ratios relative to Earth and solar system ratios (*1*). The origins of such isotopic enrichments have been attributed to precursor molecules formed in low-temperature (~10 to 200 K) interstellar clouds by grain surface and gas-phase ion-molecule reactions (*2*). After incorporation into the proto–solar system and meteorite parent bodies at about 4.5 billion years ago, the interstellar precursors reacted during a period of aqueous alteration to form some of the observed meteoritic compounds (*3*).

The finding of homologous series of organic alkyl sulfonic acids (Scheme 1A) and phosphonic acids (Scheme 1B) ($R = C_nH_{2n+1}$) in Murchison is of interest because, in meteorites, the sulfonic acids are the first well-characterized series of organic S compounds, and the phosphonic acids are the only identified organic P compounds (*4*). In addition to D/H and $^{13}C/^{12}C$ measurements, our objective was to determine if the sulfonic acids had unusual S isotope ratios. Such anomalies in the sulfonic acids, along with unusual ratios of H and C isotopes in both classes of compounds, may demonstrate that at least some meteorite organic compounds containing S and P are traceable to origins in interstellar clouds or the proto–solar nebula.



$HO-S(=O)_2-R$ $\quad$ $HO-P(=O)(OH)-R$

Scheme 1

In systems involving only two stable isotopes, such as C, H, and N, it is difficult to discriminate between ordinary mass-dependent isotopic fractionation (for example, evaporation or other kinetic isotope effects) and mass-independent processes such as nucleosynthesis or symmetry-dependent chemical mechanisms. Studying an element with four stable isotopes, such as S, removes this limitation by allowing one to observe graphically the deviation of an isotope from mass-dependent behavior (*5*, *6*). Recently, some bulk ureilite meteorites have been shown to have small ^{33}S excesses (~0.1 per mil) (*7*), and excess ^{33}S (~0.16 per mil) was found in an oldhamite (CaS) separate from the Norton County enstatite meteorite (*8*).

We examined the methyl (MSA), ethyl (ESA), isopropyl (iPSA), and *n*-propyl (nPSA) sulfonic acids. The extraction from Murchison and the separation of sulfonic acids (sulfonics) and phosphonic acids (phosphonics) from other fractions of Murchison compounds were done as described in (*9*). We achieved baseline chromatographic separation of individual sulfonics (*10*). The phosphonics are present in very small amounts in Murchison (*4*); therefore, only bulk isotopic measurements were attempted (Table 1).

In Murchison MSA, ^{33}S, ^{34}S, and ^{36}S (Table 1) are enriched relative to their abundances in various organic and inorganic phases from several meteorites (*6*–*8*, *11*). The corresponding δS values of the other sulfonics fall within a range previously observed for organic phases in Murchison and other carbonaceous chondrites (*11*). The S isotopic distribution of MSA also shows an anomalous mass-independent enrichment (*5*) in ^{33}S of $^{33}\Delta = 2.0$ per mil. The $^{33}\Delta$ value of iPSA is zero within measurement uncertainty; however, the $^{33}\Delta$ values of ESA and nPSA, although small, are anomalous (Table 1). Present measurements of ^{36}S have greater uncertainty than those of other S isotopes (Table 1) because of its low natural abundance (0.02%) coupled with the small (micromolar) sample sizes. Corresponding $^{36}\Delta$ values are of course also less certain. In MSA, the largest sample, $\delta^{36}S$, is about the value expected for a mass-dependent process, $\delta^{36}S = 2\delta^{34}S$ (*5*).

The $\delta^{13}C$ values of the sulfonics decrease with increasing carbon number, as observed with homologous series of carboxylic acids and hydrocarbons from Murchison (*12*). In relation to the known $\delta^{13}C$ values of Murchison organic compounds, the $\delta^{13}C$ values of the sulfonic acids span the range from those of the amino acids to those of the carboxylic acids (~40 to −5) (*1*).

As with the results obtained on Murchison amino acids (*13*), the D/H ratios of the sulfonics substantially exceed terrestrial ratios, indicating formation of the C–H bonds in a region that allows such D enrichment, that is, a low-temperature environment like that in interstellar clouds (*2*). In comparison with the D/H ratios of other Murchison organic compounds, the sulfonics fall in the range of the polar hydrocarbons and insoluble C (δD ~ 500 to 1000) (*1*). Because the phosphonics are present in small amounts, their isotope ratios are not corrected and are minimum values. Their D/H ratios are also above terrestrial ratios (Table 1).

Any proposed mechanism for sulfonic acid formation must account for the following observations: (i) the magnitudes of the δC, δS, and $^{33}\Delta$ values of MSA and the lower corresponding values of the other sulfonics; (ii) the similarity in structure coupled with a decline in abundance of the sulfonics with increasing carbon number (*4*), as with other homologous series of meteoritic organic compounds (*1*); and (iii) the similar D/H ratios among homologs. The second observation would seem to indicate formation of the sulfonics by the same or closely related processes. The relatively constant D/H ratios of the sulfonics could imply that unsaturated precursors (C_yS_z) to the sulfonics were formed first, followed by hydrogenation and D enrichment in a pool of nearly uniform H. The D/H values of the sulfonics as a group are nearly identical to those of Murchison polar hydrocarbons and insoluble carbonaceous material (*1*), which raises the possibility that C–H bonds of the precursors to the three groups were formed in the same pool of H.

G. W. Cooper, SETI Institute and NASA Ames Research Center, MS 239-4, Moffett Field, CA 94035, USA.
S. Chang, NASA Ames Research Center, MS 239-4, Moffett Field, CA 94035, USA.
M. H. Thiemens and T. L. Jackson, Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA 92093-0356, USA.

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*To whom correspondence should be addressed.

Table 1. Results of intramolecular measurements of stable isotopes of S, C, and H, from Murchison sulfonic acids. Uncorrected $\delta^{13}C$ values (in per mil) from a previous experiment with comparable amounts of sample are as follows: MSA, 25.4; ESA, 4.8; nPSA, 1.8; iPSA, −11.2. These are left uncorrected because of uncertainties in blank CO_2 amounts. The corresponding $^{33}\Delta$ value of MSA was 1.24 per mil (*29*). In a preliminary experiment, $\delta^{13}C$ values were also lower (*30*); however, because of refined procedures, the present sulfonics are purer isolates. The errors in measurement of samples are those of the corresponding procedural standard. Although the amount of sulfur in the procedural blank was so small that the resulting silver sulfide [see procedures in (*6*)] could not be weighed, a small amount was seen (as SO_4) on the ion chromatogram, a maximum of ~0.3 μmol. $\delta^{13}C$ values are blank corrected. The standards used for $\delta^{13}C$ and δD measurements were Pee Dee belemnite and standard mean ocean water, respectively. All isotope values are given in per mil.

Compound	Amount (μmol)	$\delta^{13}C$	δD*	$\delta^{33}S$	$\delta^{34}S$	$\delta^{36}S$	$^{33}\Delta$
R (in R-SO_3)							
CH_3 (MSA)	3.8	29.8	483	7.63	11.27	22.5	2.00
CH_3CH_2 (ESA)	1.7	9.1	787	0.33	1.13	0.8	−0.24
$CH_3CH_2CH_2$(nPSA)	0.9	−0.4	536†	0.20	1.20	2.1	−0.40
$(CH_3)_2CH$ (iPSA)	0.7	−0.9	852	0.32	0.68	2.9	−0.02
Bulk R-SO_3‡	–	6	600	–	–	–	–
Phosphonics (uncorrected)	–	−20	219	–	–	–	–
Blank	–	−21.6	−55	–	–	–	–
Standard MSA	–	−39.1	−100	0.45	0.80	2.7	0.03
Standard 1§	–	−42.2 ± 0.3	−107 ± 4	–	–	–	–
Standard 2‖	–	–	–	−0.25 ± 0.05	−0.51 ± 0.1	−1.9 ± 1.0	0.00 ± 0.05
NBS-22 standard¶	–	−29.8	−122	–	–	–	–

*The δD values are corrected for blank and exchangeable hydrogen. In contrast to C and S, less than quantitative yields of H were obtained for MSA and nPSA. However, measurements of a standard (NBS-22) with the same vacuum and combustion procedure indicated no D/H or $^{13}C/^{12}C$ fractionation, and procedural standards consisting of different amounts of MSA showed close agreement, ±4, of δD values (above). †This value is obtained after correcting for exchangeable hydrogen only. ‡From a different sample of Murchison. The matching bulk sample was lost. §Procedural standards, MSA: 1, 1, 4, and 7 μmol. ‖Procedural standards, MSA: 1 and 7 μmol. ¶$\delta^{13}C$ = −29.7, δD = −118.

The difference in S isotope composition between MSA and the other sulfonics likely arises from the differential fractionation factors associated with the formation of the individual molecules. A potential source of the ^{33}S enrichment in MSA ($^{33}\Delta = 2.0$ per mil) could be gas-phase ultraviolet (UV) irradiation of a precursor molecule such as CS_2. In the laboratory, mass-independent isotope effects have been produced by the gas-phase UV irradiation of symmetric molecules such as CS_2 (*14*), CO_2, and O_3 (*15*). The isotope effects may derive from molecular symmetry factors (*16*). In the irradiation (313-nm wavelength) of CS_2 (*14*), a ^{33}S excess of 5.3 per mil was observed in the resulting solid phase, which was characterized as $(CS_2)_x$. In that experiment, a large ^{36}S deficit was also observed, which is not the case for Murchison MSA. Recent experiments (*17*), however, have shown the process to be wavelength dependent, and the sign of the fractionations may be reversed. At present, it may only be concluded that a process capable of producing a ^{33}S excess exists in an astrophysical environment.

At the low temperatures of interstellar space, chemical reactions of the molecule CS are capable of producing compounds that could serve as sulfonic acid precursors and have mass-independent isotope anomalies resulting from gas-phase UV irradiation. CS is reactive and relatively abundant in interstellar space (*2*). In the laboratory, CS forms several molecules and an insoluble solid phase on surfaces when it is condensed at low temperatures (*18*, *19*). Molecule formation in the solid phase has been reported at temperatures as low as 33 K (*20*). The C/S ratio of the solid usually ranges from 1/1 to 5/1 (*18*). The requirements of a surface and low temperatures for CS polymerization are met by interstellar grains. In addition, CS will self-polymerize or is stable in the presence of some potentially interfering interstellar compounds. For example, CS is stable in the presence of solid methanol (*21*) and ammonia (*22*) and polymerizes in the presence of liquid methanol (*21*). In the photolysis of CS_2 (which produces CS), formation of a solid phase was not prevented by the addition of excess hydrogen and other molecules (*23*).

The CS reaction products or interstellar molecules of relevance to the present study are CS_2 (SCS), C_2S (CCS), C_2S_2 (SCCS), C_3S (CCCS), and C_3S_2 (SCCCS) (*24*). These compounds are potential precursors to the observed meteoritic sulfonic acids of the same carbon number. A high-resolution mass spectrometry study of organic matter in the Murray carbonaceous meteorite identified species of elemental compositions CS_2, C_2S, C_3S, C_3S_2, and C_3SO, in addition to many others (*25*). CS_2 is commonly seen in carbonaceous meteorites (*25*, *26*). In addition, in the present study, the unsaturated analog of ESA, vinyl sulfonic acid ($H_2C{=}C(H)SO_3^-$), was identified in an extract of a Murchison sample. These observations reinforce the possibility that the sulfonics and perhaps other interstellar carbon-chain compounds arose from unsaturated precursors, resulting from CS chemistry. Compounds of the type C_xS_2, if definitely identified in meteorites, comets, or interstellar clouds, may be more indicative of a reactive S-rich starting material like CS.

REFERENCES AND NOTES

1. J. R. Cronin and S. Chang, in *Chemistry of Life's Origins*, J. M. Greenberg, V. Pirronello, C. Mendoza-Gomez, Eds. (Kluwer, Dordrecht, Netherlands, 1993), pp. 209–258.
2. E. F. Van Dishoeck, G. A. Blake, B. T. Draine, J. I. Lunine, in *Protostars and Planets III*, E. H. Levy and J. I. Lunine, Eds. (Univ. of Arizona, Tucson, AZ, 1993), pp. 163–241.
3. T. E. Bunch and S. Chang, *Geochim. Cosmochim. Acta* **44**, 1543 (1980).
4. G. W. Cooper, W. M. Onwo, J. R. Cronin, *ibid.* **56**, 4109 (1992).
5. Also see (*6*). The stable isotopes of S have masses of 32 (95.02%), 33 (0.75%), 34 (4.21%), and 36 (0.02%) atomic mass units (amu). The deviation of the ratio of S isotopes in a sample from the standard (S in the Canyon Diablo iron meteorite) is given in parts per thousand or per mil, which is defined as $\delta^xS = \{[(^xS/^{32}S)_{sample}/(^xS/^{32}S)_{standard}] - 1\} \times 1000$, where x = 33, 34, or 36. If plotted on a three-isotope graph, normal mass-dependent fractionations should lie on the line $\delta^{33}S = 0.5\ \delta^{34}S$, because the difference between ^{33}S and ^{32}S is 1 amu and the difference between ^{34}S and ^{32}S is 2 amu, which gives 0.5 as the slope. Similarly, $\delta^{36}S = 1.97\ \delta^{34}S$. Therefore, any mass-independent isotopic anomaly in ^{33}S and ^{36}S is given by (in per mil) $^{33}\Delta = \delta^{33}S - 0.5\ \delta^{34}S$ and $^{36}\Delta = \delta^{36}S - 1.97\ \delta^{34}S$, respectively. All known terrestrial S lies on normal mass-dependent fractionation lines. The calculation of δ values for C and H is similar to that of S, that is, $\delta H = \{[(H/L)_{sample}/(H/L)_{standard}] - 1\} \times 1000$, where H and L are the heavy and light isotopes, respectively, of each element.
6. X. Gao and M. H. Thiemens, *Geochim. Cosmochim. Acta* **55**, 2671 (1991).
7. M. H. Thiemens and T. Jackson, *Lunar Planet. Sci.* **XXVI**, 1405 (1995).
8. M. H. Thiemens *et al.*, *Meteoritics* **29**, 540 (1994).
9. G. W. Cooper and J. R. Cronin, *Geochim. Cosmochim. Acta* **59**, 1003 (1995).
10. The fraction containing the sulfonics and phosphonics (*9*) was then injected into a Dionex (Sunnyvale, CA) ion chromatograph (IC) equipped with two 9 mm by 250 mm Dionex AS4-A columns and eluted with a carbonate buffer, 1.8 mM Na_2CO_3 + 1.7 mM $NaHCO_3$ (4 ml/min), to collect sulfonics and phosphonics as separate groups. At this step, nPSA separates sufficiently from the other sulfonics for collec-

tion. To collect the remaining sulfonics individually, we then reinjected the sulfonics into the IC, which was equipped with a 10 m by 100 mm Phenomenex (Torrance, CA) star-ion anion exchange column, and eluted them with a 5.4 mM Na$_2$CO$_3$ + 5.1 mM NaHCO$_3$ buffer. We separated ESA from a small amount of co-eluting sulfate by reinjecting the two compounds and eluting them with a 3.2 mM Na$_2$CO$_3$ + 3.1 NaHCO$_3$ mM buffer. Baseline separation between MSA and ESA/sulfate was ~2 min; between ESA/sulfate and iPSA, it was ~9 min, and between ESA and sulfate, it was ~1 min. After removal of the carbonate buffer with HCl, each compound was then placed in a quartz tube and dried by rotary evaporation (maximum temperature ~ 50°C). Copper oxide was then placed in each tube, and high vacuum, with mild warming (<100°C), was used for complete drying. The samples were then sealed and combusted to sulfate, CO$_2$, and H$_2$O at 800°C. The CO$_2$ and H$_2$O were collected with a procedure similar to that of Epstein *et al.* (*13*). The H$_2$O was converted to H by the method of Coleman and Moore (*27*) with a zinc catalyze from J. M. Hayes of Indiana University. The CO$_2$ and H were then analyzed with 6-60-Nuclide and 3-60-HD-Nuclide mass spectrometers. The sulfate was extracted from each tube with hydrochloric acid and prepared for S isotopic analysis as in (*6*).

11. X. Gao and M. H. Thiemens, *Geochim. Cosmochim. Acta* **57**, 3159 (1993).
12. G. Yuen, N. Blair, D. J. Des Marais, S. Chang, *Nature* **307**, 252 (1984).
13. S. Epstein, R. V. Krishnamurthy, J. R. Cronin, S. Pizzarello, G. U. Yuen, *ibid.* **326**, 477 (1987).
14. J. J. Colman, X. Xu, M. H. Thiemens, W. C. Trogler, *Science* **273**, 774 (1996).
15. K. Mauersberger, J. Morton, B. Scueler, J. Stehr, *Geophys. Res. Lett.* **20**, 1031 (1993).
16. J. Heidenreich and M. H. Thiemens, *J. Chem. Phys.* **84**, 2129 (1986).
17. X. Xu and M. H. Thiemens, unpublished data.
18. E. Moltzen, K. J. Klabunde, A. Senning, *Chem. Rev.* **88**, 391 (1988). In most of the literature, this solid phase is referred to as a "CS polymer," and we will use the terms polymer and polymerization for convenience. In the laboratory, this polymerization is highly exothermic. The heat of formation (ΔH_f) values in the range of −50 kcal/mol of CS have been estimated for the formation of CS polymers.
19. K. J. Klabunde, E. Moltzen, K. Voska, *Phosphorus Sulfur Silica Relat. Elem.* **43**, 47 (1989).
20. R. B. Bohn, Y. Hannachi, L. Andrews, *J. Am. Chem. Soc.* **114**, 6452 (1992).
21. C. M. White, thesis, University of North Dakota, Grand Forks (1974).
22. M. A. P. Hogg and J. E. Spice, *J. Chem. Soc.* **158**, 4196 (1958).
23. M. De Sorgo, A. J. Yarwood, O. P. Strausz, H. E. Gunning, *Can. J. Chem.* **43**, 1886 (1965).
24. Some reported CS reaction products are CS$_2$, C$_2$S, C$_2$S$_2$, C$_3$S, C$_3$S$_2$, CO, CO$_2$, OCS, S, S$_2$, SO, and SO$_2$. On the basis of infrared observations of low-temperature (solid phase) CS reactions, Steudel (*28*) suggested a reaction sequence where molecules of increasing carbon number are formed, leading to a polymer: xCS $\rightarrow$ CS$_2$, CCS, C$_3$S$_2$, C$_y$S$_z$ $\rightarrow$ polymer. Of the above molecules, C$_x$S$_2$ and S$_2$ (if searched for) have not been reported to occur in the interstellar medium. In addition to CS$_2$ (see text), OCS and S$_x$ are also observed in carbonaceous meteorites (*25*, *26*).
25. J. M. Hayes and K. Biemann, *Geochim. Cosmochim. Acta* **32**, 239 (1968). In the experiments, core samples of the meteorites were placed directly in the inlet of the mass spectrometer. For the identification of ions C$_2$S, C$_3$S, and C$_3$SO, a sample was heated only between 25° and 100°C for a total of 5 min. The authors give reasons as to why this temperature and time range is not severe enough to produce S compounds by decomposition of S and organics. In the case of C$_3$S$_2$, heating was between 160° and 200°C for 5 min. No theory of how such reactive compounds could have survived in the meteorite for billions of years was offered. However, if the compounds were indigenous and of the same structure as the CS condensation products (and the identified interstellar molecules), they would seem to require a special carrier in the meteorite matrix, perhaps a carbon phase such as one produced from polymerization of CS or other reactive molecules (or both).
26. M. H. Studier, R. Hayatsu, E. Anders, *ibid.* **36**, 189 (1972).
27. M. L. Coleman and M. P. Moore, *Anal. Chem.* **50**, 1594 (1978).
28. R. Steudel, *Z. Naturforsch. Teil B.* **218**, 1106 (1966).
29. G. W. Cooper, M. H. Thiemens, T. L. Jackson, S. Chang, *Meteoritics* **30**, 500 (1995).
30. G. W. Cooper and S. Chang, *Lunar Planet. Sci.* **XXVI**, 281 (1995).
31. We thank C. Moore (Arizona State University, Center for Meteorite Studies) for the sample of the Murchison meteorite; A. Tharpe for carbon isotope measurements; K. Klabunde and S. Charnley for helpful conversation; and V. Morris, N. Lerner, D. Des Marais, K. Zahnle, and L. Allamandola for comments on the manuscript. Supported by NASA grant NAGW 3551 and the Exobiology and Cosmochemistry Programs of NASA.

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Discrete Intensity Jumps and Intramolecular Electronic Energy Transfer in the Spectroscopy of Single Conjugated Polymer Molecules

David A. Vanden Bout, Wai-Tak Yip, Dehong Hu, Dian-Kui Fu, Timothy M. Swager, Paul F. Barbara*

Single-molecule fluorescence spectroscopy of a multichromophoric conjugated polymer (molecular weight ~20,000) revealed surprising single-step photobleaching kinetics and acute jumps in fluorescence intensity. These jumps were shown not to result from spectral diffusion and were attributed to fluctuations in the quantum yield of emission for the molecules. The data indicate efficient intramolecular electronic energy transfer along the polymer chain to a localized fluorescence-quenching polymer defect. The defects are created by reversible photochemistry of the polymer. These findings have implications for the use of conjugated polymers in light-emitting diode displays and sensors.

Recent developments in fluorescence microscopy have allowed for the detection, imaging, and spectroscopy of single molecules at room temperature (*1–12*). As a consequence, single-molecule spectroscopy (SMS) has moved from studies at cryogenic temperatures (*13*) to a broader range of environmental conditions. In many cases, direct information about the molecular distribution of physical quantities, rather than just the ensemble-averaged values obtained by bulk measurements, can now be obtained. Most room-temperature SMS studies have involved aromatic dye molecules that correspond to a single chromophore in a fluctuating environment and have revealed direct information on chemical and spectroscopic heterogeneity of single molecules (*4*, *14*), as well as on the dynamics of these inhomogeneities (*10*, *15*).

Here, we used SMS to study molecules that each comprise many similar chromophores, such as conjugated fluorescent polymers. Intramolecular migration of energy among these chromophores and the ultimate impact of the energy migration on photochemistry is of intense fundamental and practical interest. Conjugated polymers such as poly(*p*-phenylene vinylene) (PPV) and poly(*p*-pyridylene vinylene) (PPyV) have shown great promise for light-emitting device applications (*16*, *17*). We studied a derivatized PPV-PPyV copolymer compound with a molecular weight of ~20,000 (Fig. 1A).

Spectroscopic studies on bulk polymer materials suggest that conjugated polymer emission is often dominated by energy migration to local minima in their optical band structure (*18*). For example, anthracene-derivatized poly(*p*-phenylene-ethynylene)s in solution have been shown to selectively emit from states associated with the anthracene end groups (*19*). Although excitation diffusion along the chains in conjugated polymers is efficient, the actual optical excitation (exciton) may be localized and may have a coherence length of only a few monomer units (*20*). Thus, spectroscopic evidence of conjugated polymers suggests that their broad absorption spectra are the result of overlapping absorption bands from different segments along the polymer chain, and that their emission is strongly affected by energy migrations, often to sites remote from the absorption (*18*). This hypothesis can be

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D. A. Vanden Bout, W.-T. Yip, D. Hu, P. F. Barbara, Department of Chemistry, University of Minnesota, Minneapolis, MN 55455, USA.

D.-K. Fu and T. M. Swager, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA.

*To whom correspondence should be addressed.