

Multicomponent Synthesis of Poly(α -aminophosphine chalcogenide)s and Subsequent Depolymerization

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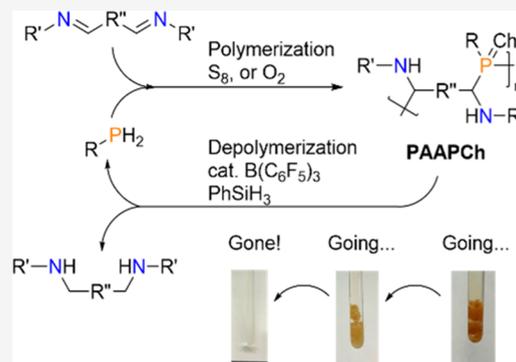


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ABSTRACT: Multicomponent reactions of primary phosphines ($R-PH_2$), diimines ($R'-N=C(H)-R-(H)C=N-R'$), and chalcogens (O_2, S_8) generate poly(α -aminophosphine chalcogenide)s (4–7) through step-growth polymerization. Characterization of the linear polymers using $^{31}P\{^1H\}$ diffusion-ordered NMR spectroscopy (DOSY) experiments aided in determining the molecular weight (M_w) of the material. Subjecting the polyphosphine oxide or sulfide to reducing conditions in the presence of a Lewis acid resulted in complete depolymerization of the polymers, quantitatively releasing the 1° phosphine and diimine (2) starting materials, with concomitant reduction of diimine to diamine (9)



INTRODUCTION

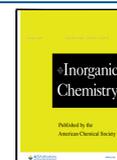
Multicomponent reactions (MCR) are indispensable tools for the synthetic chemist, as they are atom-economic, operationally simple, and highly modular procedures for generating complex molecular architectures. A recent paradigm shift toward the use of MCRs in polymer synthesis has been driven by the potential for the formation of wide libraries of specialty materials and has led to greater utilization of the Passerini, Ugi, Biginelli, Kabachnik–Fields (KF), and copper-catalyzed click reactions in polymerization and post-polymerization modification.^{1–4} The KF reaction is between a carbonyl, an amine, and a H-phosphonate to generate an α -aminophosphonate.^{5,6} Complementary to the KF transformation is the Pudovik reaction in which α -aminophosphonate is formed from an isolated imine. The KF and Pudovik reactions have been utilized in polymer development with one of the components already present on a polymer chain, followed by addition of the remaining reaction partners, such as, preformed or *in situ* generated polyaldehydes,^{7,8} polyamines,^{9–12} or polyimines (Scheme 1a–c).^{13,14} The resulting materials with pendant aminophosphonates have potential applications as flame retardant additives,¹⁴ antifouling agents,¹⁵ or heavy-metal chelators.¹⁶ Despite the suitability of the KF or Pudovik reaction to prepare polymers, none have been synthesized that contain P–C bonds in the main chain. This is likely because of the requirement to use pyrophoric, toxic, and malodorous primary phosphine ($R-PH_2$), primary phosphonate $RO-P(O)H_2$, or primary phosphine chalcogenide ($R-P(Ch)H_2$; Ch = O, S, Se) starting materials for the incorporation of phosphorus. We recently reported the reaction of 1° phosphines with imines and a chalcogen to efficiently and

cleanly generate bis- α -aminophosphine chalcogenide small molecules, which underscored the feasibility of this reaction and its potential adaptability toward polymer synthesis.¹⁷

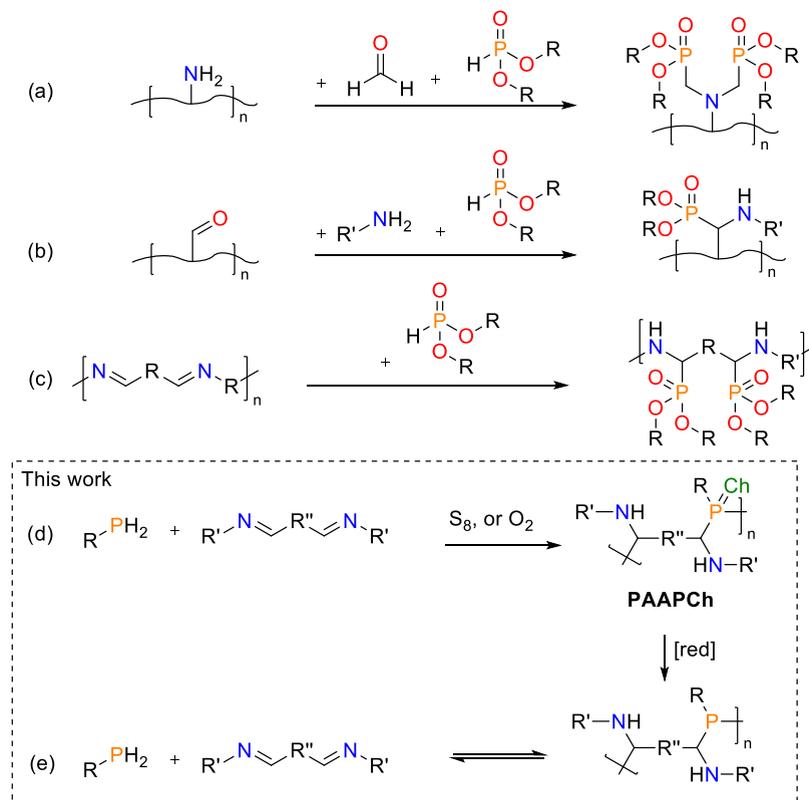
In this context, we describe the utility of the Pudovik reaction to generate poly(α -aminophosphine chalcogenide)s (PAAPCh) from a reaction between a 1° phosphine, a diimine, and a source of either S or O (Scheme 1d). These materials represent a unique class of highly modular polymers, which contain P–C bonds in the main chain and a pendant amine functional group, formed in one pot that exhibit unique physical and chemical characteristics. Since the α -aminophosphine chalcogenide functional group is part of the main chain, depolymerization was triggered by dechalcogenization, which quantitatively regenerated the primary phosphine and diamine and takes advantage of the inherent equilibrium between the generated α -aminophosphine with the 1° phosphine and imine (Scheme 1e). Through this reductive process, diimine is hydrogenated to diamine. Taken together, this represents a rare example of an inorganic polymer that can be completely depolymerized beyond polysiloxanes¹⁸ or the partial depolymerization of polyphosphazenes.¹⁹

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Scheme 1. Generation of Poly(α -aminophosphonate)s through Post-Polymerization Modification of (a) Polyamines, (b) Polyaldehydes, and (c) Polyimines; (d) Generation of Poly(α -aminophosphine chalcogenide)s (PAAPCh) through a Three-Component Reaction, and (e) Equilibrium Implicated in the Depolymerization of PAAPCh



Scheme 2. Synthesis of Linear PAAPCh 4–7 Using *i*-BuPH₂ and Corresponding Diimine and Chalcogenide. (a) H₂O₂(aq), THF, 0–40 °C, 18 h to give 4 and 5. (b) S₈, 2:1 CH₂Cl₂:Toluene, r.t., 18 h to give 6 and 7

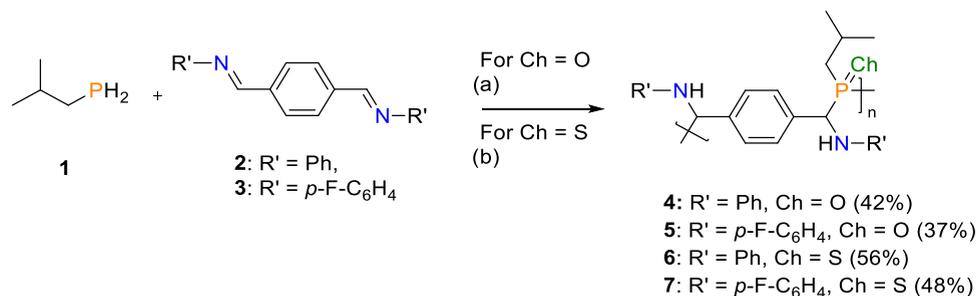
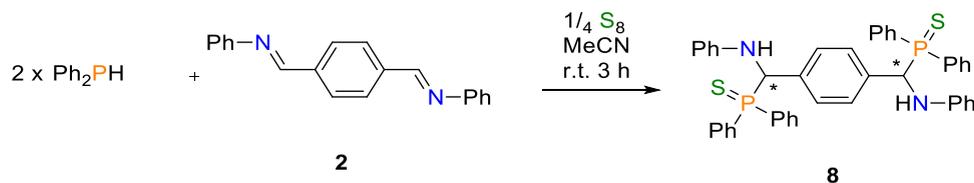


Table 1. Characterization Data for Synthesized Poly(α -aminophosphine chalcogenide)s (4–7)

compound	R'	Ch	$\delta^{31}\text{P}$ (^{19}F) ^a	M_n (g mol ⁻¹) (end cap)	M_w (g mol ⁻¹) (DOSY CDCl ₃)	T_g (°C)	$T_{98\%}$ (°C)
4	Ph	O	47.9	7400 ($n = 19$) ^b [9000 ($n = 23$)] ^c	7390 ($n = 19$)	160	223
5	<i>p</i> -F-C ₆ H ₄	O	47.9 (125.6)	4260 ($n = 10$) ^b [5300 ($n = 12$)] ^c [6800 ($n = 16$)] ^d	insoluble ^e	175	198
6	Ph	S	64.0	5600 ($n = 14$) ^b [7100 ($n = 17$)] ^c	13,900 ($n = 34$)	109	199
7	<i>p</i> -F-C ₆ H ₄	S	64.0 (125.4)	7800 ($n = 17$) ^b [7100 ($n = 16$)] ^c [5700 ($n = 13$)] ^d	2400 ($n = 5$)	134	190

^aCDCl₃. ^b³¹P{¹H}. ^c¹H. ^d¹⁹F{¹H}. ^eS/N ratio under gradient was insufficient for accurate DOSY analysis.

Scheme 3. Synthesis of a Small-Molecule Analogue 8 from Ph₂PH, 2, and S₈

RESULTS AND DISCUSSION

The reaction between *i*-butyl phosphine (1), a *para*-substituted *N,N'*-(terephthalylidene)bis(aniline) (2; 3), and H₂O₂(aq) was performed in a 1:1:1 ratio at 0 °C in THF under gentle heating to 40 °C after addition of the oxidant (Scheme 2; Note a). The reaction was monitored by ³¹P{¹H} NMR spectroscopy, where numerous signals were observed throughout the course of the reaction that corresponded to 2° and 3° P(III) species and their corresponding P(V) oxidized counterparts. The sulfide analogues were prepared by dropwise addition of a toluene solution of S₈ to a CH₂Cl₂ solution of 1 and 2 or 3 (Scheme 2; Note b). To ensure high conversion that is required to obtain high molecular weight (*M_w*) polymers from a step-growth polymerization process, the reaction was carried out at the highest concentration achievable with the starting precursors.²⁰ Relevant solvents were selected to maintain good solubility of oligomers throughout the course of the reaction, as well as miscibility with the aqueous H₂O₂. Only *N*-aryl imines were selected since prior KF polymerization studies established that *N*-alkyl imines are insufficiently electrophilic to afford high *M_w* polymers.^{7,13} Our preliminary experiments using R' = *n*-Bu diimines resulted in large quantities (≥30%) of the corresponding P(Ch)Ch–H species, even with careful control of addition, and precise stoichiometry. This ultimately shows that the oxidation and P–H bond addition reactions are competing processes. Careful control of the quantity of oxidant to the reaction mixture was required, as overoxidation to the P(Ch)Ch–H species promotes chain termination. After 18 h, a broad signal dominated at δ_p = 47.9 for the oxides (Table 1: 4, 5 and Figures S19 and S22) and δ_p = 64.0 for the sulfides (Table 1: 6, 7 and Figures S26 and S29). These chemical shifts match closely with the corresponding bis-*α*-aminophosphine chalcogenides (δ_p for Ch = O; 47.1–49.5 for Ch = S; 63.7–65.3).¹⁷ All polymers were isolated by precipitation from CH₂Cl₂ or THF as pale orange/yellow powders in moderate yield (37–56%).

Comprehensive characterization of the afforded polymers was carried out including multinuclear NMR spectroscopy, diffusion-ordered spectroscopy (DOSY), Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and gel permeation chromatography (GPC) analysis (see Table 1). FTIR analysis of the generated polymers supports the reduction of the C=N bond to a single bond, from the disappearance of the C=N signal (1612 cm⁻¹), and the formation of a P=Ch bond (Ch = O, 1152 cm⁻¹; Ch = S, 540 cm⁻¹) is also observed in the final products, closely matching those of the small-molecule models (Figures S39–S43).¹⁷

Thermogravimetric analysis (TGA) measured for the phosphine oxide polymers showed a higher onset of decomposition, at 223 and 198 °C for compounds 4 and 5 (Figures S5 and S6), respectively, as compared to the corresponding sulfide derivatives at 199 and 190 °C for 6 and 7 (Figures S7 and S8). DSC analysis measured for phosphine oxide polymers 4 and 5 displayed *T_g* values of 160 and 175 °C,

respectively (Figures S9 and S10). The phosphine sulfide polymers 6 and 7 showed *T_g* values of 109 and 134 °C, respectively (Figures S11 and S12). The *T_g* values for the phosphine oxide polymers are higher than their corresponding sulfide analogues overall, and the *T_g* values for the p-F derivative are greater than those for the unfunctionalized aryl ring. We hypothesized that this is the effect of hydrogen bonding interactions between the P=O and N–H functional groups, as observed in the solid-state structure of the bis-*α*-amino-phosphine oxide small molecule (CCDC: 2167769).¹⁷

GPC analyses of polymers 4–7 show low *M_w* species ranging from 1000 to 3000 g mol⁻¹. These values correspond to short-length oligomers (*n* = 3–8; Figures S45–S48), which would be expected to display molecular properties rather than those of a macromolecule. Oligomers exhibit narrow melting points, and are contrary to the broad *T_g* values observed for compounds 4–7. The GPC analysis was inconsistent with *M_w* data obtained by both end-group analysis and DOSY (*vide infra*), likely because of the interactions between the polar P=Ch (EN; P = 2.19, O = 3.44, S = 2.58) and N–H functional groups and the stationary phase of the GPC column. Similar incompatibility of inorganic polymers with GPC columns has been acknowledged.^{21,22} The notable low solubility of 4–7 likely also biases the *M_w* values toward the more soluble oligomeric molecules. This prompted the analysis of chain lengths by alternative experimental means. The heteroatom-rich nature of polymers 4–7 facilitated *M_n* determination by end-group analysis using ¹H, ³¹P{¹H}, and ¹⁹F{¹H} NMR spectroscopy (i.e., 5 and 7). Determination by ³¹P{¹H} NMR spectra exploited the distinct signals observed for P(Ch)Ch–H or R₂P(Ch)H end-groups *vs* in-chain phosphine chalcogenide. Analysis by ¹H NMR spectroscopy involved relative integration of terminal imine or aldehyde signals to alkyl *i*-Bu groups of the chain. A similar method was employed by ¹⁹F{¹H} spectroscopy since unique signals were found for terminal C=N-(*p*-F-C₆H₄) as compared to in-chain C–N(H)-(p-F-C₆H₄) units. The *M_n* values obtained for 4–7 *via* the three different NMR-active nuclei are in good agreement with each other, with discrepancies only ranging from two to six repeat units (Table 1: 4–7). To corroborate the molecular weight data obtained by end-group analysis, ³¹P{¹H} DOSY NMR experiments were carried out. Optimized diffusion parameters of 4, 6, and 7 in CDCl₃ were obtained, and the diffusion coefficients were determined to be 5.37 × 10⁻¹⁰, 3.89 × 10⁻¹⁰, and 9.55 × 10⁻¹⁰ m² s⁻¹, respectively (Figures S1–S4). This corresponds to molecular weights of 7400, 13,900, and 2400 g mol⁻¹ when referenced to a DOSY PMMA calibration curve in CDCl₃ (Figure S1). The poor solubility of sample 5 resulted in a S/N ratio that was insufficient for DOSY analysis. The *M_w* value of the phosphine oxide polymer 4 is lower than that of the phosphine sulfide polymer 6 (4: 7400 g mol⁻¹, 6: 13,900 g mol⁻¹) and is a result of the insolubility of the oxide materials, which forced 4 to precipitate from solution once a particular chain length was reached. In contrast, polymer 6 remains soluble throughout the course of its preparation, which

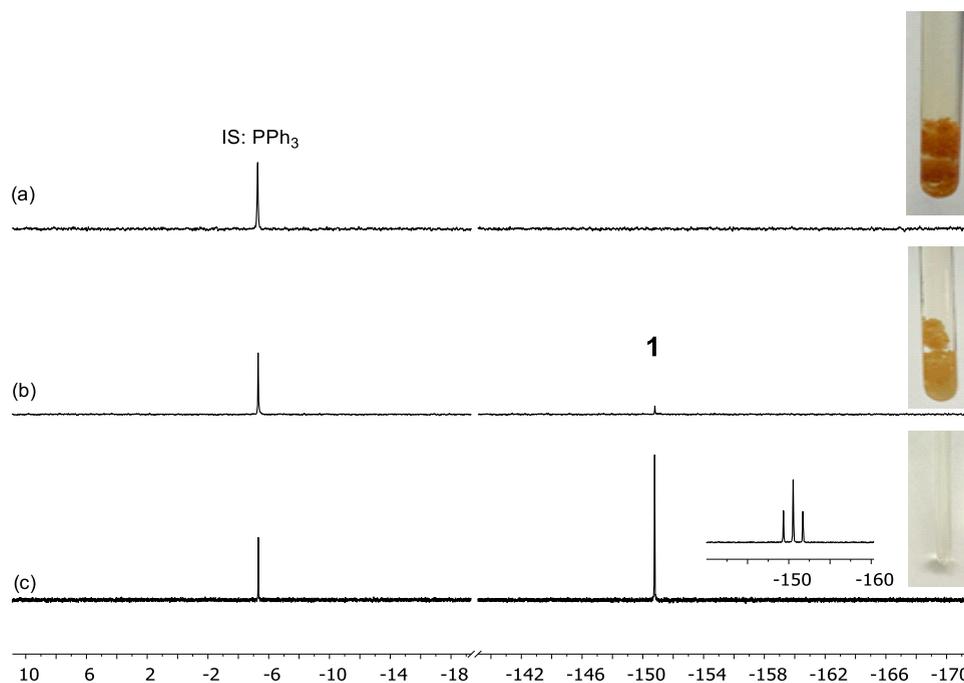
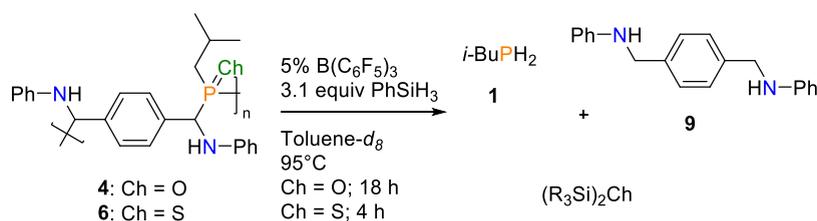
Scheme 4. Depolymerization of 4 and 6 by Dechalcogenation Mediated by 5 mol % B(C₆F₅)₃ and PhSiH₃ to Generate *i*-BuPH₂ and 9


Figure 1. ³¹P{¹H} NMR spectra (toluene-*d*₈) of the depolymerization reaction of 4 along with photos of the physical samples (right) (a) starting insoluble polymer shows no resonances. (b) After 40 min of reaction time, formation of *i*-BuPH₂ (1) was observed. (c) After 18 h of reaction time, substantial formation of *i*-BuPH₂ (1) was observed, with a completely homogeneous sample. Inset: ³¹P NMR spectrum showing splitting of the signal into a triplet.

allowed for greater chain growth. The poor solubility of phosphine oxides 4 and 5 hinders the NMR and GPC analysis as measurements are only representative of the soluble, shorter polymer chains. Therefore, all techniques, 1D NMR, DOSY, and GPC, underestimate the molecular weight of both 4 and 5. To assist in the validation of the DOSY measurements, small molecule 8 was prepared using diimine 2, Ph₂PH, and S₈ (Scheme 3). The resulting diffusion coefficient of 1.67 × 10⁻⁹ m² s⁻¹ corresponded to a *M*_w of 697 g mol⁻¹ and is in good agreement with the calculated *M*_w of 8 (720 g mol⁻¹).

Depolymerization of polymers is an increasingly urgent area in need of development in order to combat the long-term environmental impact of these materials. Intentional design and incorporation of depolymerizable functional groups is an established concept, but largely in its infancy, especially for polymers with inorganic elements as part of the main chain.^{23,24} In the case of 4–7, the α-aminophosphine chalcogenide can pose as a handle by which to activate depolymerization. Reduction of the P(V) center to P(III) reestablishes the equilibrium between the P(III) α-aminophosphine with the corresponding starting 1° phosphine and imine.^{17,25–27} Deoxygenation of 4 was achieved by using 5 mol % B(C₆F₅)₃ and 3.1 stoichiometric equivalents of PhSiH₃ at 95 °C in toluene

(Scheme 4). The polymer sample was insoluble in toluene, and no resonance was observed in the ³¹P{¹H} spectrum at *t* = 0. Over the course of the reaction (18 h), the suspension becomes completely homogeneous since the depolymerization products (*i.e.*, the starting materials for the polymer) are soluble (Figure 1, images). Monitoring the reaction by ³¹P{¹H}, ³¹P, and ¹H spectroscopies revealed the fate of the polymer (Figure 1, NMR spectra). After 40 min of heating, a new resonance appeared at –150 ppm in the ³¹P{¹H} spectrum (³¹P, *t*, ¹J_{P–H} ≈ 190 Hz) that indicated the clear regeneration of *i*-BuPH₂. This was corroborated using FTIR spectroscopy of the reaction mixture that showed a strong vibration at 2150 cm⁻¹, characteristic of a P–H bond (Figure S44).²⁸ A known amount of internal standard was added to the sample tube (PPh₃, 0.2 mM in toluene) and this allowed for the quantification of *i*-BuPH₂ (1) that was produced during the depolymerization reaction. From a 50 mg sample, 13.2 mg of 1 was regenerated, corresponding to 26% mass of the overall sample, which is in very good agreement with the theoretical relative mass of 23% of 1 in polymer sample 4. The presence of excess silane, combined with Lewis acid, can hydrosilylate the corresponding imine and subsequently hydrolyze to generate the amine.²⁹ This was supported by an examination of the ¹H NMR spectrum, where a closer look was

warranted because no signals corresponding to the starting imine at $\delta = 8.06$ were observed (Figure S36). Rather, signals corresponding to the generated methylene of bis-amine **9** were present as a singlet at $\delta = 3.91$. This assignment was corroborated through the independent synthesis of **9** in which spectroscopic signatures exactly matched the species observed in the reaction mixture. Applying the same methodology to the phosphine sulfide polymer **6** likewise incited depolymerization to **1** and the corresponding diamine product **9**. The depolymerization of **6** was completed after 4 h of reaction time (Figure S38).

CONCLUSIONS

We reported the multicomponent step-growth polymerization reaction between a primary phosphine (R-PH₂), a diimine, and a chalcogen to afford poly(α -aminophosphine chalcogenide)s (PAAPCh) of up to 13,900 g mol⁻¹. The resulting polymers are an example of a polymer containing phosphorus as part of the main chain. This was possible by taking advantage of an understanding of fundamental redox chemistry of P(III) and P(V) derivatives, specifically in the stabilization of the α -aminophosphine by chalcogenization of phosphorus. The unique structure and related reactivity of the α -aminophosphine chalcogenide functional group allowed for the material to be successfully depolymerized under reducing conditions. In principle, the regenerated phosphine can be separated and recycled to regenerate the polymer or for a new purpose. In a similar vein, the diimine could be utilized a second time; however, the depolymerization reaction established ideal Frustrated Lewis Pair (FLP) conditions under which reduction of the C=N bond occurs. A chain growth polymerization method for preparation would afford far more control over the M_w , enabling tuning of the chain lengths and structure–property relationship determination.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.3c02039>.

Synthetic procedures as well as characterization data, and NMR, ESI-MS, FTIR, DOSY, GPC, TGA, and GPC (PDF)

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Author Contributions

J.-W.L.-I. was responsible for the design and execution of the experimental research, the acquisition and analysis of characterization data, and writing the original drafts. M.J.W. was responsible for the data acquisition of the DOSY experiments. J.B.G. and J.J.N. were responsible for review and editing processes. J.M.B. and P.J.R. were responsible for funding acquisition (with J.B.G. and J.J.N.), project conceptualization, supervision, project administration, review, and editing.

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Notes

The authors declare no competing financial interest.

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