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COMMUNICATION
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N-Heterocyclic carbene stabilized parent sulfenyl, selenenyl, and tellurenyl cations (XH^+, X = S, Se, Te)

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COMMUNICATION

Spacer-Tuned Diphosphine Dioxides as Preorganised Co-Ligands for Synergistic Lithium Extraction with β-Diketonates†

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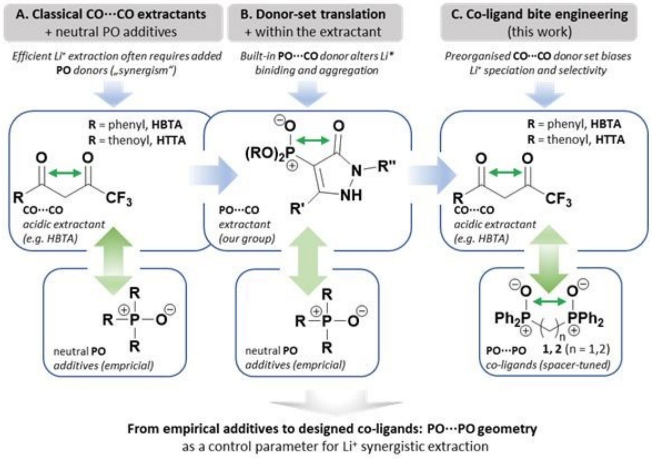
Synergistic liquid-liquid extraction (LLE) of Li$^+$ commonly relies on β-diketonates in combination with neutral phosphine oxides such as tri-*n*-octylphosphine oxide (TOPO), yet the co-ligand is typically treated as an empirical additive rather than a design element. Here we show that commercially available diphosphine dioxides, featuring a preorganised PO···PO donor set and a spacer-defined bite, act as powerful co-ligands for Li$^+$ extraction with 3-benzoyl-1,1,1-trifluoroacetone (HBTA) under mild pH conditions. Compared to TOPO, the best-performing PO···PO co-ligand enhances Li$^+$ transfer while suppressing Na$^+$/K$^+$ co-extraction, consistent with altered solution speciation and stoichiometry. These results establish a chelating co-ligand (PO···PO) as a simple, modular strategy to control synergy in Li$^+$ extraction systems based on classical CO···CO extractants such as HBTA.

Lithium has become a strategically vital element for the global economy because rechargeable lithium-ion batteries (LIBs) underpin consumer electronics, electric mobility, and grid-level storage.[1] The projected growth of lithium demand, driven largely by the expanding EV market, intensifies the need for scalable and selective Li recovery from diverse resources.[2,3] Brine-based sources (salt-lake brines, geothermal brines, and oilfield brines) are particularly attractive due to their large reserves and comparable low operating costs,[4] but lithium separation remains difficult because Li$^+$ is present at low concentration and competes with the abundant alkali and alkaline-earth metal ions (Na$^+$/K$^+$/Mg^{2+}/Ca^{2+}).[5]



Scheme 1 Three design strategies for synergistic Li$^+$ extraction: (**A**) CO···CO extractants + neutral P=O additives, (**B**) PO···CO donor-set translation (our earlier work), and (**C**) this work: spacer-tuned PO···PO diphosphine dioxides for co-ligand bite engineering.

Among available separation technologies, liquid–liquid extraction (LLE) is appealing because it is operationally simple and compatible with continuous processing.[6] Industrially relevant Li$^+$ extraction typically relies on acidic extractants, including organophosphorus acids such as bis(2-ethylhexyl)phosphate (D2EHPA)[7,8] as well as β-diketones/acylpyrazolones and related O,O-chelators.[9-11] A key practical feature shared across many of these systems is that efficient Li$^+$ transfer into the organic phase often requires neutral organophosphorus additives (e.g., phosphine oxides such as tri-*n*-octylphosphine oxide (TOPO)[12–15] or Cyanex 923)[16], i.e. synergistic extraction. In D2EHPA-based systems, aggregation (including dimeric extractant motifs)[17] and adduct formation with neutral donors are frequently invoked to rationalize performance enhancements, whereas for O,O-chelators the co-ligand can act as an additional donor that stabilizes charge-neutral Li-containing assemblies in the organic phase. Despite their widespread use, the molecular origin of synergism is still commonly treated empirically rather than as a tuneable structural parameter.

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Supplementary Information available: [Methods and procedures, detailed synthetic procedure, copy of NMR and additional characterisation data, detailed procedure and used equation for the solvent extraction experiments; crystallographic details. See DOI: 10.1039/x0xx00000x

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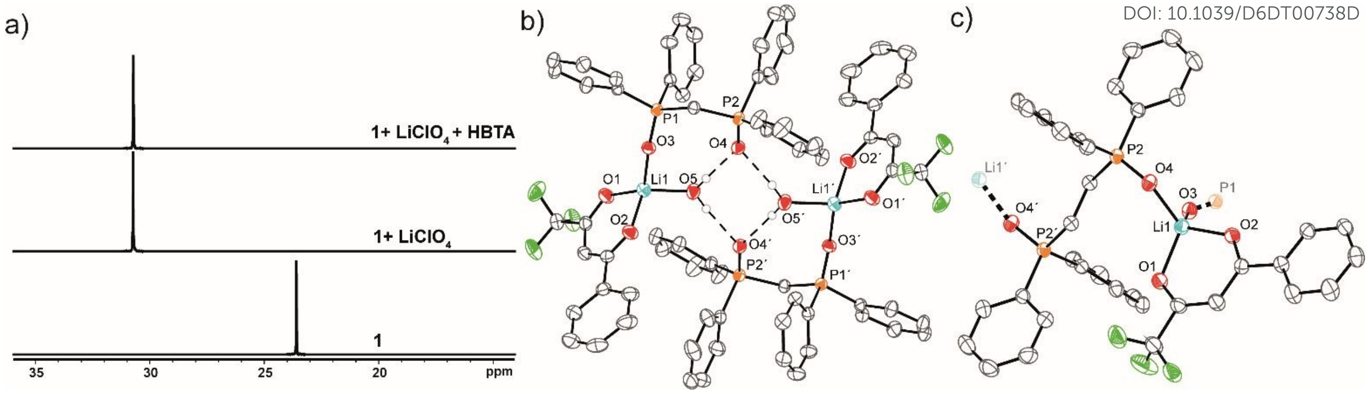

Fig. 1. Cutout of $^{31}P\{^{1}H\}$ spectra of **1** in CH_2Cl_2 before and after contact with $LiClO_4$, and for mixture of HBTA and **1** after contact with $LiClO_4$ (a), molecular structures of [Li(BTA)(**1**)·H_2O] linked via reciprocal hydrogen bonds of the coordinated water (b) and a repeating unit of $\{[Li(BTA)(\mathbf{2})]\cdot(H_2O)_{0.75}\cdot(DCM)_{0.09}\}_n$ (c) (all carbon hydrogen atoms and solvate molecules are omitted for clarity, thermal ellipsoids are displayed at 50 % probability, hydrogen bonds displayed as dashed lines).

In this context, **Scheme 1** summarises three conceptually distinct design strategies for synergistic Li^+ extraction: **(A)** classical CO···CO extractants that rely on neutral P=O additives as empirical enhancers; **(B)** donor-set translation within the extractant itself (PO···CO), which embeds a phosphoryl donor as a built-in structural element; and **(C)** co-ligand bite engineering (PO···PO), where the extractant remains unchanged but synergism is tuned through a geometry-encoded co-ligand family.

In our earlier work, we demonstrated that 4-phosphoryl pyrazolones introduce a deliberate donor-set translation from classical CO···CO chelation to PO···CO binding, enabling Li^+ recognition and extraction under mild conditions through well-defined di- and trinuclear Li motifs in the presence of neutral co-ligands (TBP/TBPO/TOPO).[18,19] Building on this concept, we now ask whether synergism can be made even more “designable” by shifting the neutral component itself from a generic additive to a geometry-encoded co-ligand family: PO···PO donors with controlled PO···PO separation (e.g., CH_2 vs CH_2CH_2 spacers). In this way, the co-ligand becomes a structural handle that can bias aggregation, stabilize specific Li stoichiometries, and ultimately tune extraction efficiency and selectivity. Guided by this concept, we selected two commercially accessible, spacer-defined diphosphine dioxides as minimal PO···PO co-ligands (**1** and **2**, n = 1,2; **Scheme 1C**) to test whether co-ligand geometry alone can modulate Li^+ speciation and, in turn, extraction performance when the acidic extractant is kept constant. Diphosphine dioxides of this type have been reported previously and used in transition-metal coordination chemistry,[20,21] yet their potential as preorganised O-donor co-ligands for Li^+ recognition and synergistic LLE has not been explored. We therefore combined **1** and **2** with the benchmark β-diketones 3-benzoyl-1,1,1-trifluoroacetone (HBTA) and compared their performance against the widely used monodentate additive TOPO under mild pH conditions.

Receptors **1** and **2** were obtained in high yield (>95%) by oxidizing the respective bisphosphines with H_2O_2 following adapted literature procedures (ESI†).[20,21] Their ability to transfer Li^+ into an organic phase was first probed by contacting CH_2Cl_2 solutions of diposphine oxides (with and without the β-diketones) with solid $LiClO_4$, followed by multinuclear NMR analysis of the supernatant (**Figure 1a**; full data in **Figure S15–S19**, ESI†). For **1**, the ^{31}P single resonance at δ = 23.6 ppm shifted downfield to δ = 30.7 ppm upon contact with $LiClO_4$. The absence of resolved splitting is consistent with a symmetric interaction of the two PO groups of **1** with Li^+ on the NMR timescale. The addition of HBTA to the organic phase did not induce an additional marked ^{31}P shift (**Figure 1a**), suggesting that the immediate PO environment in the dominant Li-containing species remains similar under these conditions. In the corresponding ^{7}Li NMR spectra, no Li^+ signal was detected in CH_2Cl_2 after contacting with $LiClO_4$ alone, whereas addition of **1** enabled detection of a broad resonance at δ = 0.85 ppm ($\nu_{1/2}$ = 3.6 Hz, **Figure S16,** ESI†), confirming Li^+ transfer into the organic phase. Addition of HTBA did not produce a meaningful change in the Li^+ chemical shift within experimental resolution (**Figure S16**, ESI†). In line with our earlier observations for related Li^+/O-donor assemblies,[19] this does not exclude subtle changes in Li^+ speciation and any such effects are better assessed by stoichiometry and structural data (*vide infra*).

Comparable experiments with **2** likewise showed a downfield shift of the ^{31}P resonance from δ = 30.9 to 33.3 ppm when contacted with $LiClO_4$ (**Figure S18**, ESI†). Upon addition of HBTA, a further small upfield shift to δ = 31.5 ppm was observed, consistent with a modest change in the PO environment in the Li-containing species. In ^{7}Li NMR, Li^+ was detected in the organic phase only in the presence of **2**, giving a broad resonance at δ = 0.74 ppm ($\nu_{1/2}$ = 3.4 Hz, **Figure S19**, ESI†). The addition of HBTA resulted in a very broad resonance at δ = 0.94 ppm ($\nu_{1/2}$ = 22 Hz) consistent with a noticeable change in the Li environment in the presence of **2** and HBTA.

To identify plausible coordination motifs underlying the observed synergy, Li^+ complexes were synthesised from HBTA, **1** or **2**, and $LiOH\cdot H_2O$ in CH_2Cl_2 (ESI†). Single crystals suitable for X-ray analyses of [Li(BTA)(**1**)·H_2O] were obtained by slow diffusion of pentane into a saturated CH_2Cl_2, while crystals of $\{[Li(BTA)(\mathbf{2})]\cdot(H_2O)_{0.75}\cdot(DCM)_{0.09}\}_n$ formed by slow evaporation of from toluene/CH_2Cl_2.

In both structures (**Figure 1b, c**), Li^+ is four-coordinate and bound by the O,O-chelate of deprotonated BTA^-, forming the

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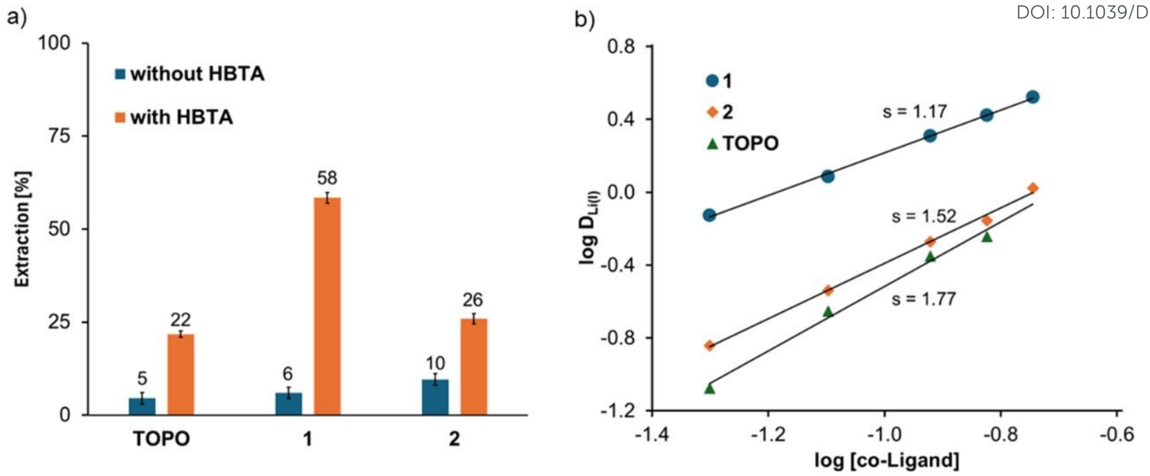

Fig. 2. a) Percent extraction of Li(I) of the co-ligands **1**, **2** and TOPO in the absence and presence of HBTA and b) Li(I) extraction in dependence of the concentration of co ligand. Experimental conditions: [LiCl] = 0.01 M, [NH_4Cl] = 0.1 M, pH = 8.5 (Tris/HCl buffer), a) [co-ligand] = 0.1 M, b) [co-Ligand] = 0.05 - 0.18 M, [HBTA] = 0.1 M in $CHCl_3$, 300 K, extraction time = 12 h.

expected six-membered chelate ring. In [Li(BTA)(**1**)·H_2O], the coordination sphere is completed by one phosphoryl oxygen from **1** and one bound water molecule (**Figure 1b**). The second PO group of **1** does not bind to Li^+ directly, but engages in hydrogen bonding with the coordinated water; discrete mononuclear units are linked in the lattice via reciprocal hydrogen bonds. In contrast, **2** bridges between Li centres through both phosphoryl oxygen atoms, generating repeating [Li···OP–$(CH_2)_2$–PO···Li] connections and an extended 1D chain (**Figure 1c**). The Li–O(P) bond lengths to the phosphine oxide donors span a comparatively wide range (1.874(3) and 1.937(3) Å), while the Li–O distances to the BTA-derived O atoms are 1.929(3) and 1.901(3) Å, consistent with an overall more distorted tetrahedral coordination environment in the polymeric motif. By comparison, in [Li(BTA)(**1**)·H_2O] the four Li–O contacts are much more uniform (Li–O1 1.914(3), Li–O2 1.915(3), Li–O3 1.919(2), Li–O5 1.910(2) Å), in line with a more regular local coordination sphere for the discrete complex.

The performance of **1** and **2** as PO···PO co-ligands was evaluated in LLE using HBTA as the acidic O,O-chelator, with TOPO included as benchmark (ESI†). Because practical brines and many real feed streams are acid to slightly basic, we selected pH 8.5 as a representative condition (Tris/HCl buffer). Under these conditions, control experiments confirmed that HBTA is required for Li^+ transfer into the organic phase, consistent with its role as the charge-balancing anion in the extracted Li-containing species. With HBTA present, co-ligand identity has a decisive impact: **1** affords 58% Li^+ extraction, substantially higher than **2** (26%) and TOPO (22%) under otherwise identical conditions (**Figure 2a**). These results directly support the central premise of **Scheme 1C**: co-ligand geometry/bite is a strong handle to tune synergy, even when the acidic extractant (HBTA) is unchanged.

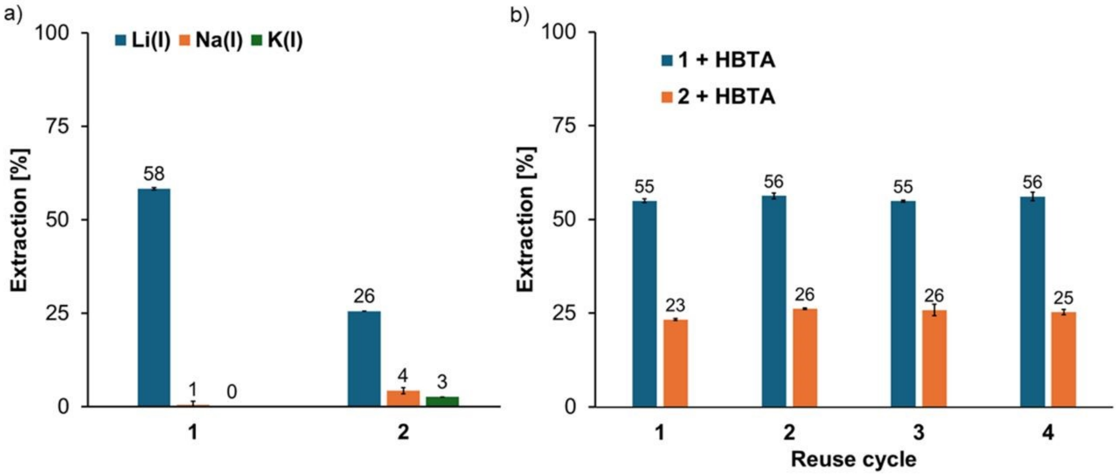

Fig. 3 a) Percent extraction of Li(I), Na(I), and K(I) competitively extracted and b) Reusability test for liquid-liquid extraction of Li(I) by **1** and **2** in presence of HBTA. Conditions for a): [LiCl] = 0.01 M, [NaCl] = 0.01 M, [KCl] = 0.01 M, [NH_4Cl] = 0.1 M, pH = 8.5 (Tris/HCl buffer, 12h and for b): [LiCl] = 0.01 M, [NH_4Cl] = 0.1 M, pH = 8.5 (tris/HCl buffer), [**1**] = 0.1 M, [**2**] = 0.1 M [HBTA] = 0.1 M in $CHCl_3$, 300 K, overnight; for stripping: 0.5 M HCl, 300 K, 1 h.

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To probe the composition of Li-containing species in the organic phase, slope analyses were performed (ESI†, Eq. S4–S6), plotting log$D$–log[co-ligand]$_{(org)}$ (**Figure 2b**). For TOPO, a slope of ~2 agrees with literature[22] and is consistent with formation of [Li(BTA)(TOPO)$_2$] under the extraction conditions. In contrast, **1** gives a slope of ~1, indicating a dominant 1:1 Li$^+$:co-ligand contribution, in line with the solid-state formulation [Li(BTA)(**1**)·H_2O] (noting that coordinated water may be replaced by solvent and/or additional donors in the organic phase). For **2**, an intermediate slope of ~1.5 suggests mixed stoichiometries (between predominant 1:1 and 1:2 Li$^+$:**2** contributions), consistent with the structural tendency of **2** to connect Li centres (chain propagation) while still allowing termination by additional donors in solution to form organo-soluble adducts.

To assess selectivity under competitive conditions relevant to brines, LLE experiments were conducted with equimolar Li$^+$/Na$^+$/K$^+$ in the aqueous phase (**Figure 3a**). The Li$^+$ extraction efficiencies remain essentially unchanged (58% for **1**, 26% for **2**), while co-extraction of Na$^+$ and K$^+$ is very low: for **1** only trace transfer (<1%) is detected, whereas **2** shows slightly higher, but still minor, Na$^+$/K$^+$ extraction (ca. 3–4%). These data highlight that **1** combines high Li$^+$ transfer with strong suppression of Na$^+$/K$^+$ co-extraction under the chosen conditions.

Recyclability was evaluated over four extraction/stripping cycles. After Li$^+$ loading at pH 8.5, stripping with 0.5 M HCl (V(aq):V(org) = 1:1) releases Li$^+$ quantitatively and regenerates the organic phase. Across four cycles, extraction efficiencies remain stable (ca. 55–56% for **1** and 24–27% for **2**; **Figure 3b**), and stripping is essentially complete in each cycle (**Table S1**, ESI†), demonstrating operational robustness.

In addition, selected follow-up experiments were conducted with **1** in the presence of HBTA. In experiments examining the effect of pH, a clear dependence was observed, as expected. While extraction is negligible at a pH of 6 and below, a steady increase to 69% extraction of Li$^+$ at a pH of 9 is observed (**Figure S21**, ESI†). Initial studies on the influence of Mg^{2+} and Ca^{2+} show that these ions are preferentially extracted. (**Table S2**, ESI†)

In summary, we demonstrate that simple diphosphine dioxides **1** and **2** act as effective PO···PO co-ligands for synergistic Li$^+$ extraction with the benchmark β-diketone HBTA under mild pH conditions. Solid-state structures reveal distinct coordination outcomes: **1** supports discrete Li-containing units, whereas **2** readily generates chain-like Li···O(P) connectivity. In LLE, these differences translate into markedly different performance: **1** provides substantially enhanced Li$^+$ transfer relative to **2** and TOPO and strongly suppresses Na$^+$/K$^+$ co-extraction. Presumably, the shorter CH_2 spacer in **1** allows the formation of discrete Li$^+$ complexes in solution, which leads to increased extraction. Slope analyses support altered stoichiometry/speciation relative to TOPO. Collectively, these results establish chelating co-ligand with spacer-defined PO···PO donors as a straightforward and modular strategy to tune synergism in Li$^+$ extraction systems built on classical CO···CO-type acidic extractants. In further experiments the separation of Li$^+$ from earth alkali metals such as Mg^{2+} and Ca^{2+} should be in focus to determine whether separation via pH regulation is possible, as reported in the literature.[19]

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Conflicts of interest

There are no conflicts to declare.

Data availability

Crystallographic data for [Li(BTA)(1)·H_2O] and {[Li(BTA)(2)]·$(H_2O)_{0.75}$·$(DCM)_{0.09}$}$_n$ have been deposited with the CCDC (2538695 and 2538696). Syntheses and analyses, NMR spectra, crystallographic details, details for the LLE investigations have been included as part of the ESI.†.

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