Supporting Information for

Probing Solvent Effects on Mixed Aggregates Associating a Chiral Lithium Amide and n-BuLi by NMR: From Structure to Reactivity

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Table S3: D-FW analysis of $^1$H-DOSY data of 4a/$n$-BuLi complex in THF$_{d8}$ at 195K

1. Instrumental Considerations

NMR spectra were recorded at 195K and 250K on a Bruker AVIII 500 spectrometer operating at 500.13 MHz for $^1$H, 125.13 MHz for $^{13}$C and 73.60 MHz for $^6$Li. Experiments were run under TopSpin (version 2.1, Bruker Biospin, Karlsruhe) with a BBFO($^1$H,$X$) probe and a z gradient coil giving a maximum gradient of 50 G cm$^{-1}$. $^1$H and $^{13}$C chemical shifts were referenced to the solvent residual signals (for Et$_2$O$_{d10}$ at $\delta$ 3.34 ppm ($^1$H) and 14.5 ppm ($^{13}$C), for THF$_{d8}$ at $\delta$ 1.73 ($^1$H) and 25.31 ppm($^{13}$C)). Lithium spectra were referenced to external 0.3 M $^6$LiCl solution in THF$_{d8}$ ($\delta$ 0.0).
2. NMR spectra of amine 3a and amide 4a in Et₂O<sub>d10</sub>

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Figure S2. $^{13}$C{$^1$H} NMR spectra of 3a (top) and 4a (bottom) in Et$_2$O$_{d10}$ at 195K
Figure S3. $^1$H, $^{13}$C-HMQC spectrum of 4a in Et$_2$O$_{d10}$ at 195K

Figure S4. $^1$H, $^{13}$C-HMBC spectrum of 4a in Et$_2$O$_{d10}$ at 195K
Figure S5. $^1$H,$^1$H-COSY spectrum of 4a in Et$_2$O at 195K
Figure S6. $^6$Li NMR spectra of $n$-BuLi (top) and 4a (bottom) in Et$_2$O$_{d10}$ at 195K

Figure S7. $^6$Li NMR spectra with resolution enhancement (GB = 0.1, LB = –0.5) (top) and proton H1 selective decoupling (bottom) of 4a in Et$_2$O$_{d10}$ at 250K
Figure S8. $^1$H,$^1$H-NOESY (mixing time $\tau_m = 0.60$ s) spectrum of 4a in Et$_2$O$_{d10}$ at 250K.
Figure S9. $^1$H-DOSY spectrum of 4a in Et$_2$O$_{d10}$ at 195K

Figure S10. Decay curves of $^1$H-DOSY for Internal References [COE (a), HMDS (b), SQA (c)] and 4a (d) in Et$_2$O$_{d10}$ at 195K
Table S1 D-FW analyses of $^1$H-DOSY data of 4a in Et$_2$O$_{d10}$ at 195K

<table>
<thead>
<tr>
<th>compound</th>
<th>FW (g mol$^{-1}$)</th>
<th>LogFW</th>
<th>D (m$^2$ s$^{-1}$)</th>
<th>logD</th>
<th>predicted FW (g mol$^{-1}$)</th>
<th>Error (%)</th>
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<tbody>
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$^a$: the predicted FW is referred to an unsolvated dimer [([4a])$_2$].
3. NMR spectra of amine 3a and amide 4a in THF-$d_8$

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Figure S18. $^1$H-DOSY spectrum of 4a in THF$_{d8}$ at 195K

Figure S19. Decay curves of $^1$H-DOSY for Internal References [COE (a), HMDS (b), SQA (c)], monomer 4a (d) and C$_2$-dimer 4a (e) in THF$_{d8}$ at 195K
Table S2. D-FW analyses of $^1$H-DOSY data of 4a in THF$_{d8}$ at 195K

<table>
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<tr>
<th>compound</th>
<th>FW (g mol$^{-1}$)</th>
<th>LogFW</th>
<th>D (m$^2$ s$^{-1}$)</th>
<th>logD</th>
<th>predicted FW (g mol$^{-1}$)</th>
<th>Error (%)</th>
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<td>C$_2$-dimer 4a</td>
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</table>

$^a$: the predicted FW is referred to a trisolvated monomer [(4a)$_3$+3THF]. $^b$: the predicted FW is referred to an unsolvated dimer [(4a)$_2$]. $^c$: the predicted FW is referred to a monosolvated dimer [(4a)$_2$+THF].
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Figure S24. $^1$H,$^{13}$C-HMBC spectrum of 4a + $n$-BuLi in THF$_{d8}$ at 195K
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<thead>
<tr>
<th>Compound</th>
<th>FW (g mol$^{-1}$)</th>
<th>LogFW</th>
<th>D (m$^2$ s$^{-1}$)</th>
<th>logD</th>
<th>predicted FW (g mol$^{-1}$)</th>
<th>Error (%)</th>
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<tr>
<td>COE</td>
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$^a$: the predicted FW is referred to a trisolvated monomer [(4a) + 3THF]. $^b$: the predicted FW is referred an unsolvated dimer [(4a)$_2$]. $^c$: the predicted FW is referred to a disolvated mixed dimer [(4a+n-BuLi) + 2THF].

correlation between logD and logFW

$y = -0.78x - 8.384$

$R^2 = 0.9949$