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Electronic Supplementary Information

Experimental evidences for hypercoordination in triorganotelluronium halides with 2-(Me_2NCH_2)C_6H_4 groups

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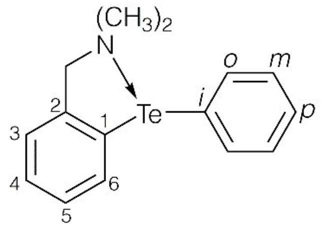

Scheme S1 Numbering scheme for NMR resonance assignments.

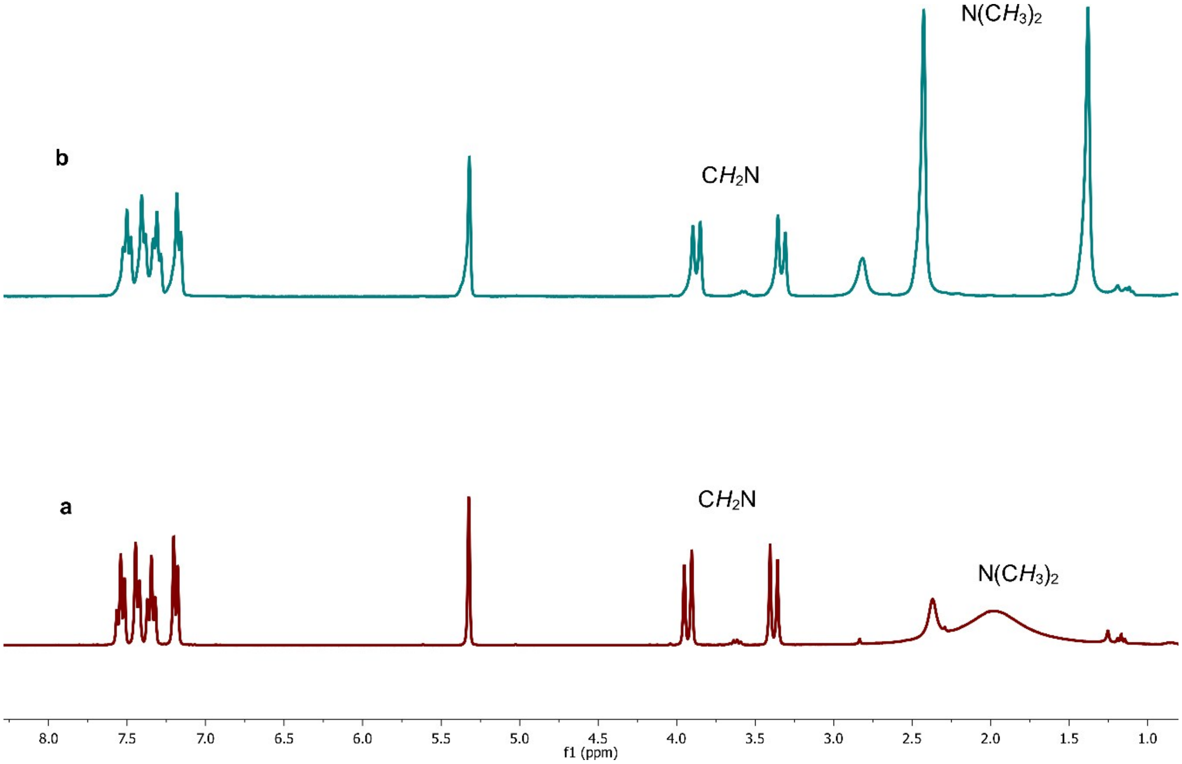

Figure S1. The ^{1}H NMR (CD_2Cl_2, 300.11 MHz) spectra of $[\{2\text{-}(Me_2NCH_2)C_6H_4\}_3Te]^+Cl^-$ (**7**) at +20 °C (**a**), and –30 °C (**b**).

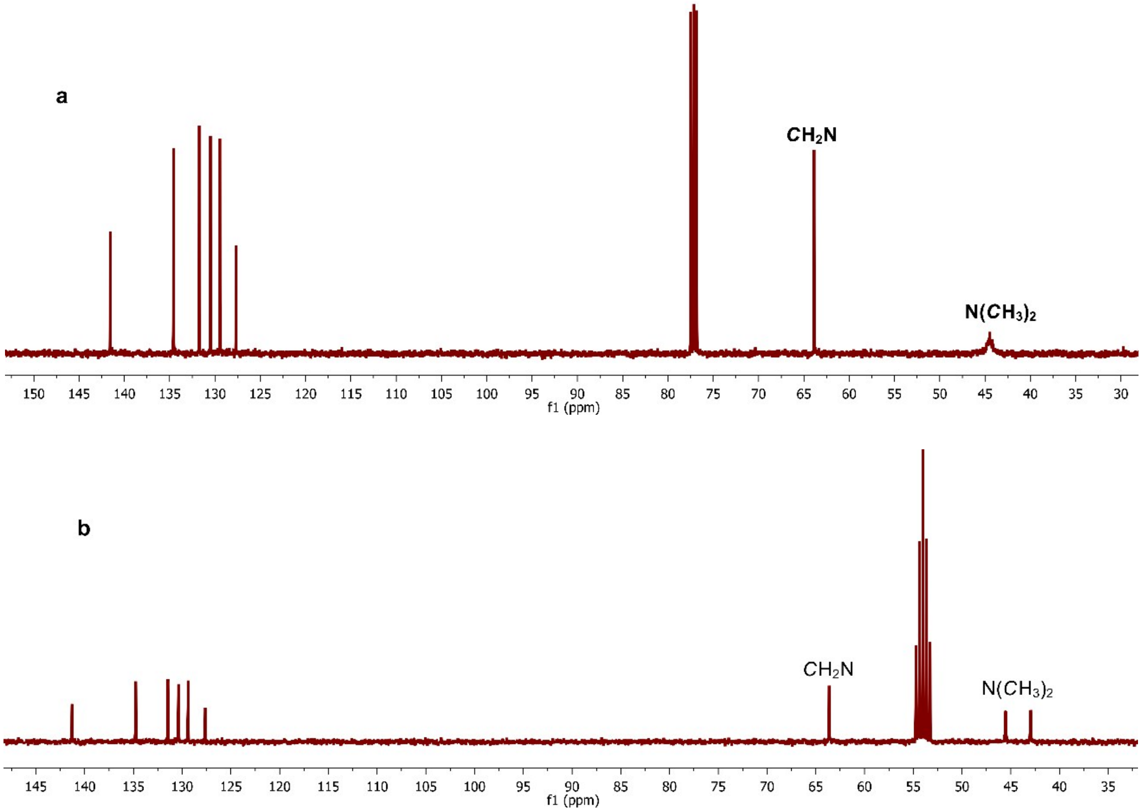

Figure S2. The ^{13}C NMR (75.46 MHz) spectra of $[\{2\text{-}(Me_2NCH_2)C_6H_4\}_3Te]^+Cl^-$ (**7**) at +20 °C (in $CDCl_3$) (**a**), and –30 °C (CD_2Cl_2) (**b**).

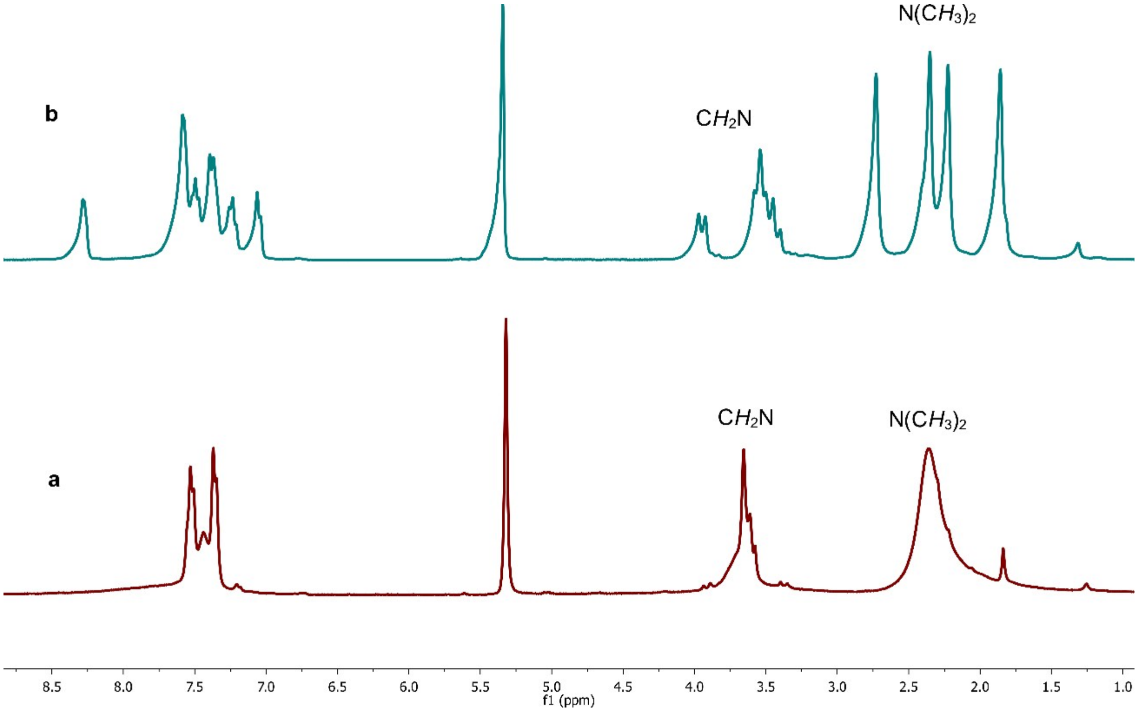

Figure S3. The ^{1}H NMR (CD_2Cl_2, 300.11 MHz) spectra of $[\{2\text{-}(Me_2NCH_2)C_6H_4\}_2(OH)Te]^+Cl^-$ (**10**) at +20 °C (**a**), and –80 °C (**b**).

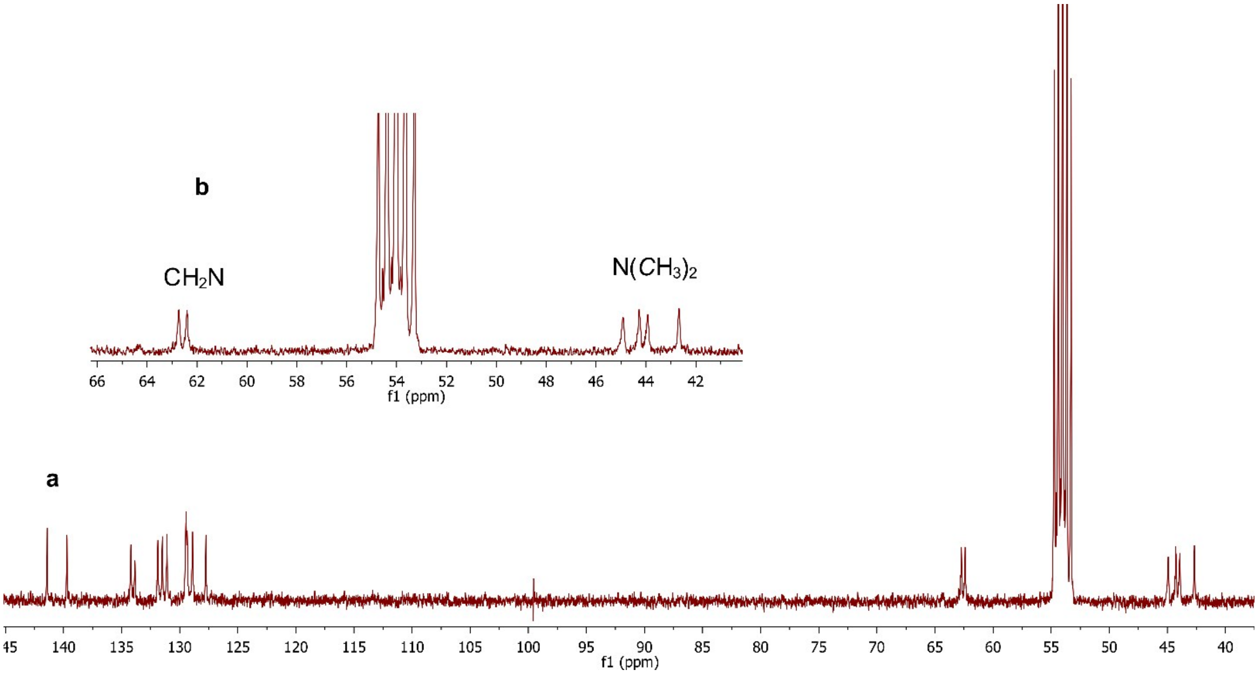

Figure S4. The ^{13}C NMR (CD$_2$Cl$_2$, 75.46 MHz) spectrum of [{2-(Me$_2$NCH$_2$)C$_6$H$_4$}$_2$(OH)Te]$^+$Cl$^-$ (**10**) at –80 °C (**a**), and expended aliphatic region (**b**).

$[\{2\text{-}(Me_2NCH_2)C_6H_4\}Ph_2Te]^+Cl^-$ (1)

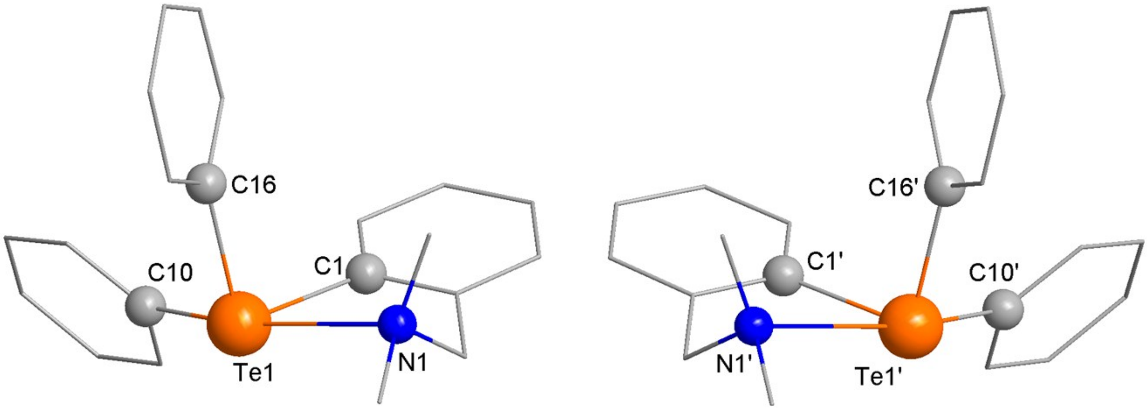

Figure S5. Structures of the $(A_{\mathrm{Te1}})(pR_{\mathrm{N1}})$ (*left*) and $(C_{\mathrm{Te1'}})(pS_{\mathrm{N1'}})$ (*right*) cations in the crystal of **1** (for clarity, hydrogen atoms are not shown) [symmetry equivalent atoms (*2–x, 2–y, 1–z*) are given by "prime"].

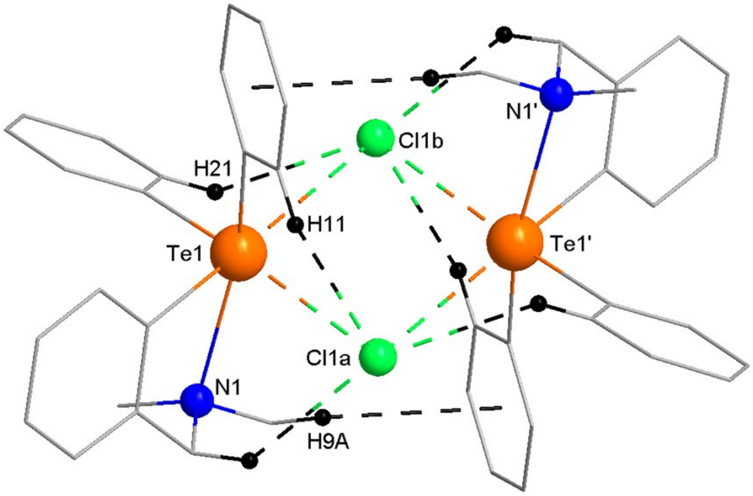

Figure S6. Dinuclear association through interactions between $(A_{\mathrm{Te1}})(pR_{\mathrm{N1}})$ and $(C_{\mathrm{Te1a}})(pS_{\mathrm{N1a}})$ cations and chloride anions in the crystal of **1**, supported by additional $C–H_{\mathrm{methyl}}\cdots\pi$ (Ph_{centroid}) and C–H···Cl contacts (only hydrogen atoms involved in contacts with heavier atoms or aromatic rings are shown) [symmetry equivalent atoms (*2–x, 2–y, 1–z*), (*1+x, 1+y, z*) and (*1–x, 1–y, 1–z*) are given by "prime", "a" and "b", respectively].

- interatomic distances	$C(9)–H(9A)_{\mathrm{methyl}}\cdots Ph_{\mathrm{centroid}}\{C(10')\text{-}C(15')\}$	2.91 Å	($\gamma = 5.5°$)
	$C(11)–H(11)_{\mathrm{phenyl}}\cdots Cl(1a)$	2.78 Å	$\sum r_{\mathrm{vdW}}(Cl,H)$ 3.01 Å
	$C(21)–H(21)_{\mathrm{phenyl}}\cdots Cl(1b)$	2.86 Å	
	$C(7)–H(7A)_{\mathrm{methylene}}\cdots Cl(1a)$	2.97 Å	

A 3D supramolecular architecture is formed through additional C–H···Cl contacts between dinuclear units in the crystal of **1** [symmetry equivalent atoms (*x, 1+y, z*) and (*1–x, 2–y, 1–z*) are given by "d" and "e", respectively]:

$C(14)–H(14)_{\mathrm{phenyl}}\cdots Cl(1d)$	2.78 Å
$C(20)–H(20)_{\mathrm{phenyl}}\cdots Cl(1e)$	2.92 Å

$[\{2\text{-}(Me_2NCH_2)C_6H_4\}Ph_2Te]^+Cl^-\cdot 0.5CH_2Cl_2$ ($\mathbf{1}\cdot 0.5CH_2Cl_2$)

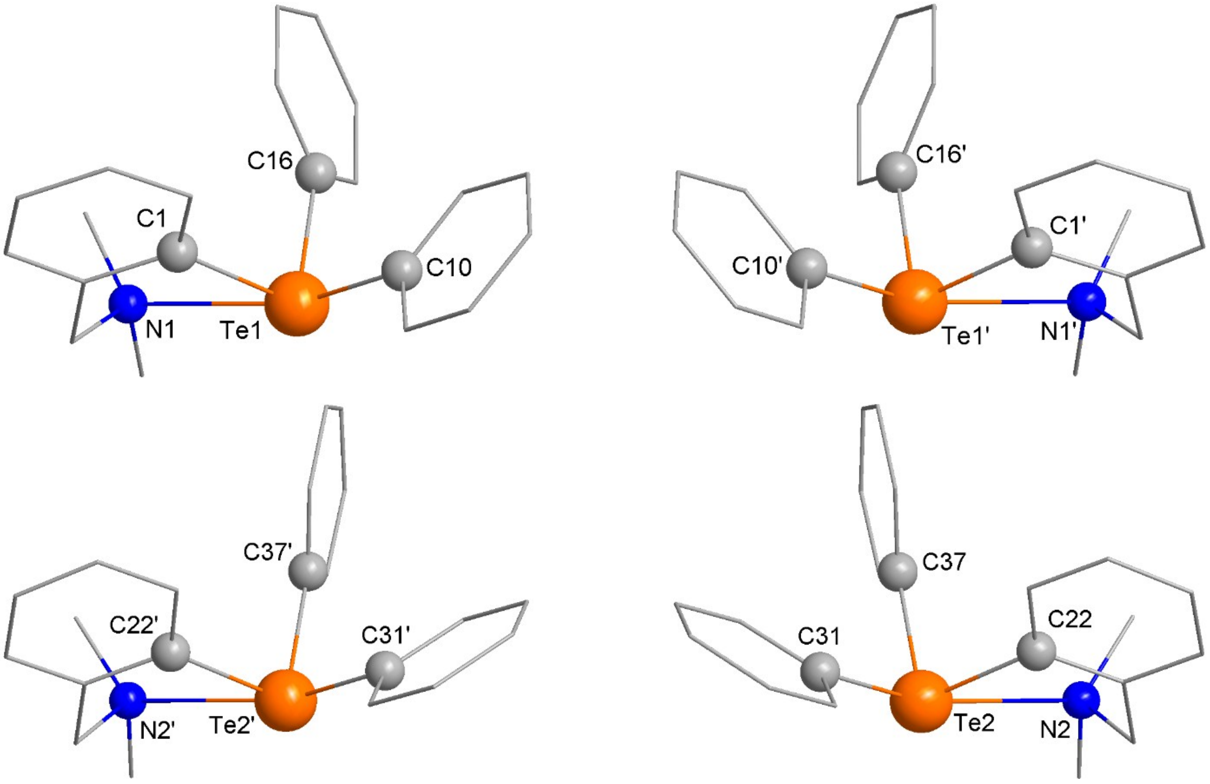

Figure S7. Structures of the (A_{Te1})(pR_{N1}) (*left, up*) / ($C_{\mathrm{Te1'}}$)($pS_{\mathrm{N1'}}$) (*right, up*) and ($A_{\mathrm{Te2'}}$)($pR_{\mathrm{N2'}}$) (*left, down*) / (C_{Te2})(pS_{N2}) (*right, down*) cations in the crystal of **1**·0.5CH$_2$Cl$_2$ (for clarity, hydrogen atoms are not shown) [symmetry equivalent atoms (*1–x, 1–y, 1–z*) are given by “prime”].

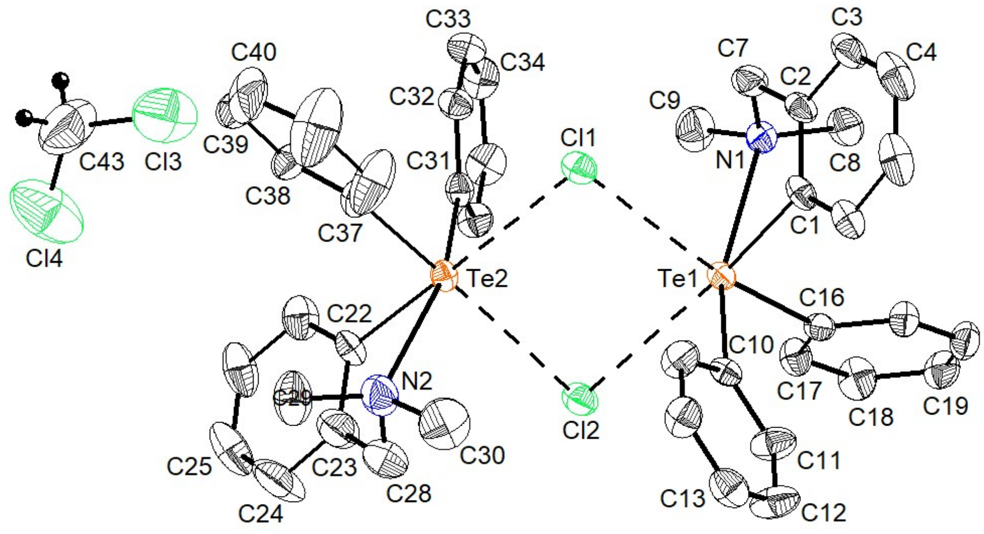

Figure S8. Dinuclear association through interactions between (A_{Te1})(pR_{N1}) and (C_{Te2})(pS_{N2}) cations and chloride anions in the crystal of **1**·0.5CH$_2$Cl$_2$. Thermal ellipsoids are drawn at 25% probability (hydrogen atoms are omitted for clarity).

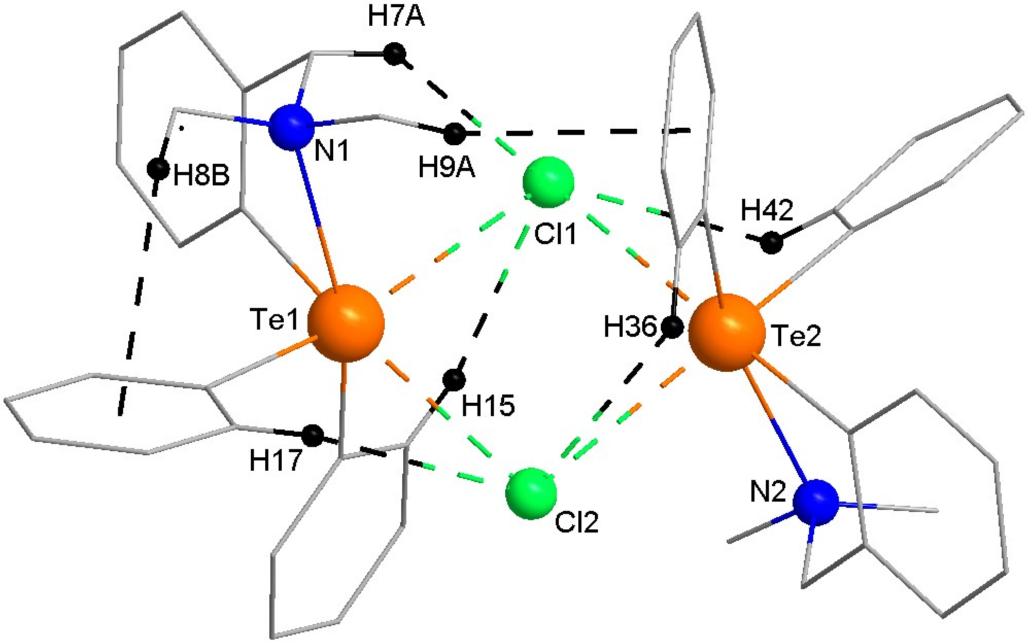

Figure S9. Dinuclear association through interactions between (A_{Te1})(pR_{N1}) and (C_{Te2})(pS_{N2}) cations and chloride anions in the crystal of **1**·0.5CH_2Cl_2, supported by additional C–H$_{\text{methyl}}$···π (Ph$_{\text{centroid}}$) and C–H···Cl contacts (only hydrogen atoms involved in contacts with heavier atoms or aromatic rings are shown; the CH_2Cl_2 molecule is omitted).

- interatomic distances	C(9)–H(9A)$_{\text{methyl}}$···Ph$_{\text{centroid}}${C(31)-C(36)}	2.72 Å	($\gamma = 4.5°$)
	C(8)–H(8B)$_{\text{methyl}}$···Ph$_{\text{centroid}}${C(16)-C(21)}	2.92 Å	($\gamma = 10.0°$)
	C(15)–H(15)$_{\text{phenyl}}$···Cl(1)	2.76 Å	$\sum r_{\text{vdW}}$(Cl,H) 3.01 Å
	C(17)–H(17)$_{\text{phenyl}}$···Cl(2)	2.84 Å	
	C(7)–H(7A)$_{\text{methylene}}$···Cl(1)	2.90 Å	
	C(36)–H(36)$_{\text{phenyl}}$···Cl(2)	2.90 Å	
	C(42)–H(42)$_{\text{phenyl}}$···Cl(1)	2.93 Å	

A 3D supramolecular architecture is formed through additional C–H···π (Ar$_{\text{centroid}}$) and C–H···Cl contacts between dinuclear units in the crystal of **1**·0.5CH_2Cl_2 [symmetry equivalent atoms (*1.5–x, 0.5+y, 1.5–z*), (*2–x, 1–y, 2–z*), (*–0.5+x, 1.5–y, –0.5+z*), (*2–x, 1–y, 1–z*), (*–1+x, y, z*) and (*0.5+x, 1.5–y, –0.5+z*) are given by “a”, “b”, “c”, “d”, “e” and “f”, respectively].

C(25)–H(25)$_{\text{aryl}}$···Ar$_{\text{centroid}}${C(1a)-C(6a)}	2.97 Å	($\gamma = 22.5°$)
C(12)–H(12)$_{\text{phenyl}}$··· Ar$_{\text{centroid}}${C(16b)-C(21b)}	3.06 Å	($\gamma = 7.2°$)
C(43)–H(43B)$_{\text{CH2Cl2}}$···Cl(2c)	2.61 Å	
C(3)–H(3)$_{\text{aryl}}$···Cl(1d)	2.74 Å	
C(38)–H(38)$_{\text{phenyl}}$···Cl(3)$_{\text{CH2Cl2}}$	2.83 Å	
C(35)–H(35)$_{\text{phenyl}}$ ···Cl(1e)	2.90 Å	
C(40)–H(40)$_{\text{phenyl}}$ ···Cl(2f)	2.96 Å	

$[\{2\text{-}(\mathrm{Me_2NCH_2})\mathrm{C_6H_4}\}\mathrm{Ph_2Te}]^+\mathrm{I}^-$ (3)

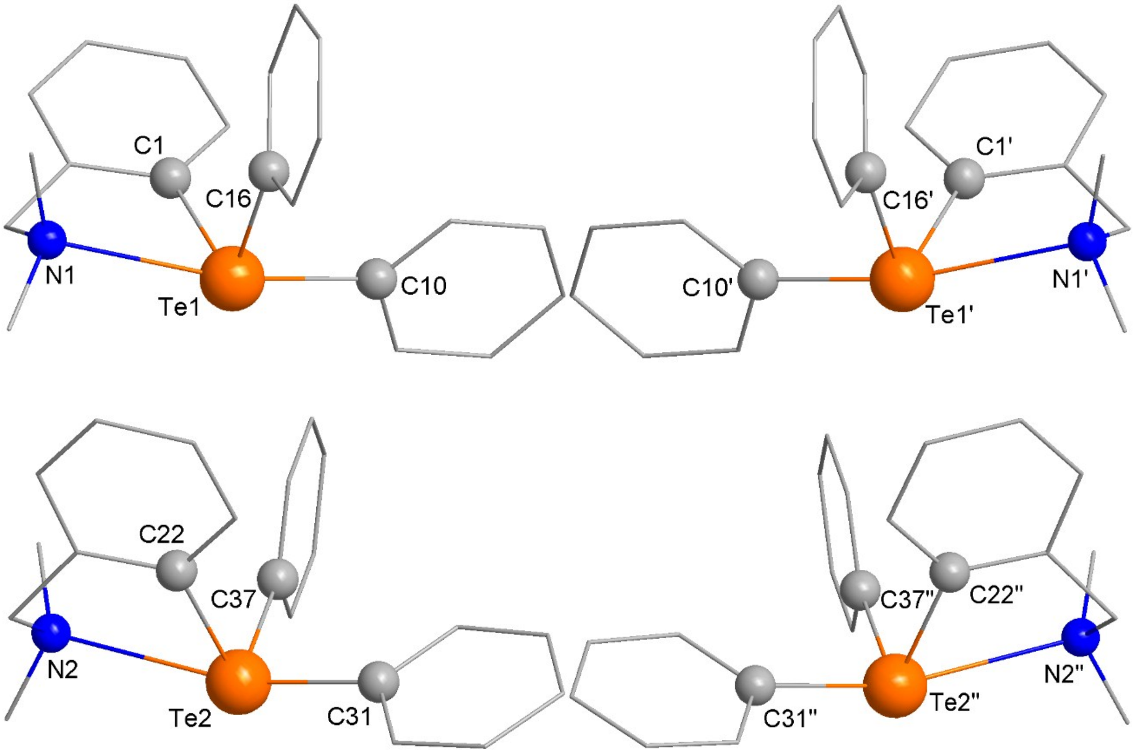

Figure S10. Structures of the $(C_{\mathrm{Te1}})(pS_{\mathrm{N1}})$ (*left, up*) / $(A_{\mathrm{Te1'}})(pR_{\mathrm{N1'}})$ (*right, up*) and $(A_{\mathrm{Te2}})(pR_{\mathrm{N2}})$ (*left, down*) / $(C_{\mathrm{Te2''}})(pS_{\mathrm{N2''}})$ (*right, down*) cations in the crystal of **3** (for clarity, hydrogen atoms are not shown) [symmetry equivalent atoms (*–x, 1–y, –z*) and (*1–x, –y, 1–z*) are given by "prime" and "double prime", respectively].

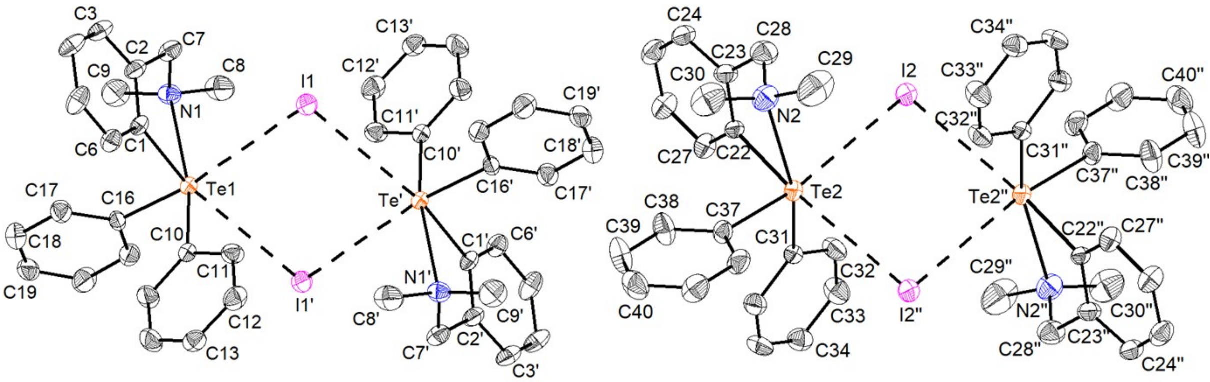

Figure S11. Dinuclear associations through interactions between pairs of $(C_{\mathrm{Te1}})(pS_{\mathrm{N1}})$ / $(A_{\mathrm{Te1'}})(pR_{\mathrm{N1'}})$ or $(A_{\mathrm{Te2}})(pR_{\mathrm{N2}})$ / $(C_{\mathrm{Te2''}})(pS_{\mathrm{N2''}})$ cations and iodide anions in the crystal of **3**. Thermal ellipsoids are drawn at 25% probability (hydrogen atoms are omitted for clarity) [symmetry equivalent atoms (*–x, 1–y, –z*) and (*1–x, –y, 1–z*) are given by "prime" and "double prime", respectively].

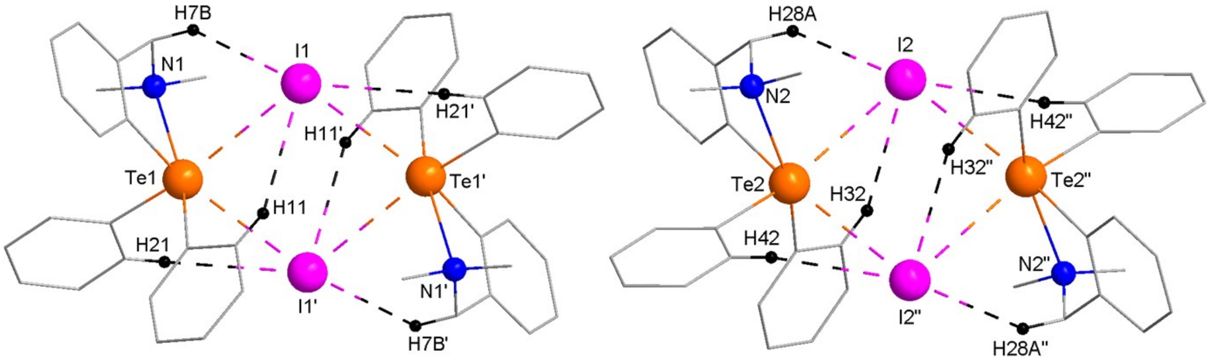

Figure S12. Dinuclear associations through interactions between pairs of $(C_{\mathrm{Te1}})(pS_{\mathrm{N1}})$ / $(A_{\mathrm{Te1'}})(pR_{\mathrm{N1'}})$ or $(A_{\mathrm{Te2}})(pR_{\mathrm{N2}})$ / $(C_{\mathrm{Te2''}})(pS_{\mathrm{N2''}})$ cations and iodide anions in the crystal of **3**, supported by additional C–H···I contacts (only hydrogen atoms involved in contacts with heavier atoms) [symmetry equivalent atoms (*–x, 1–y, –z*) and (*1–x, –y, 1–z*) are given by "prime" and "double prime", respectively].

- interatomic distances	$C(11)–H(11)_{\mathrm{phenyl}}\cdots I(1)$	3.11 Å	$\sum r_{\mathrm{vdW}}(I,H)$ 3.35 Å
	$C(21)–H(21)_{\mathrm{phenyl}}\cdots I(1')$	3.24 Å	
	$C(7)–H(7B)_{\mathrm{methylene}}\cdots I(1)$	3.27 Å	
	$C(32)–H(32)_{\mathrm{phenyl}}\cdots I(2)$	3.12 Å	
	$C(42)–H(42)_{\mathrm{phenyl}}\cdots I(2'')$	3.20 Å	
	$C(28)–H(28A)_{\mathrm{methylene}}\cdots I(2)$	3.22 Å	

A 3D supramolecular architecture is formed through additional C–H···I contacts between dinuclear units in the crystal of **3** [symmetry equivalent atoms (*x, 0.5–y, 0.5+z*) and (*–x, 0.5+y, –0.5–z*) are given by "a" and "b", respectively].

$C(35a)–H(35a)_{\mathrm{phenyl}}\cdots I(2)$	3.21 Å
$C(25b)–H(25b)_{\mathrm{aryl}}\cdots I(1)$	3.24 Å
$C(19a)–H(19a)_{\mathrm{phenyl}}\cdots I(2)$	3.30 Å

$[\{2\text{-}(Me_2NCH_2)C_6H_4\}_2PhTe]^+Cl^-\cdot H_2O$ ($\mathbf{4}\cdot H_2O$)

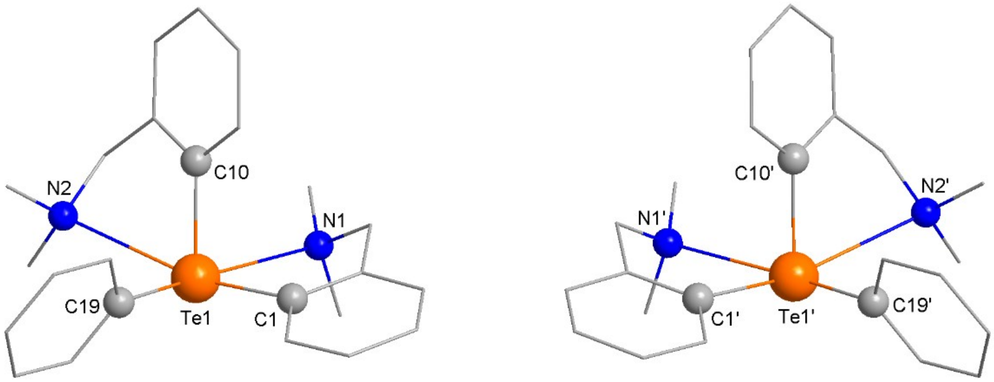

Figure S13. Structures of the (C_{Te1})(pR_{N1},pS_{N2}) (or Λ_{Te1}) (*left*) and ($A_{Te1'}$)($pS_{N1'}$,$pR_{N2'}$) (or Δ_{Te1}) (*right*) cations in the crystal of **4**·H_2O (for clarity, hydrogen atoms are not shown) [symmetry equivalent atoms (*1–x, 1–y, –z*) are given by "prime"].

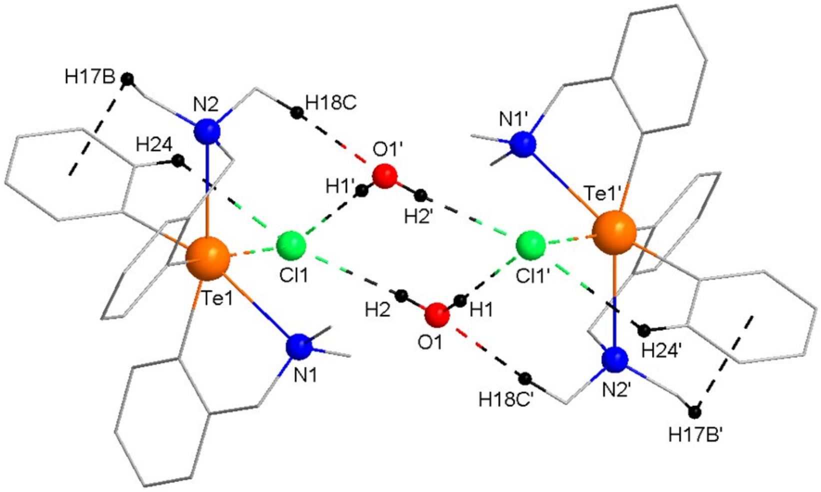

Figure S14. Dinuclear association through interactions between (C_{Te1})(pR_{N1},pS_{N2}) and ($A_{Te1'}$)($pS_{N1'}$,$pR_{N2'}$) cations and chloride anions in the crystal of **4**·H_2O, supported by additional C–$H_{methyl}\cdots\pi$ ($Ph_{centroid}$), C–$H_{phenyl}\cdots$Cl and C–$H_{methyl}\cdots$O contacts (only hydrogen atoms involved in contacts with heavier atoms or aromatic rings are shown) [symmetry equivalent atoms (*1–x, 1–y, –z*) are given by "prime"].

- interatomic distances	C(17)–H(17B)$_{methyl}\cdots$Ph$_{centroid}$\{C(19)-C(24)\}	3.00 Å ($\gamma = 13.2°$)	
	C(24)–H(24)$_{phenyl}\cdots$Cl(1)	2.91 Å	$\sum r_{vdW}$(Cl,H) 3.01 Å
	O(1)–H(2)$\cdots$Cl(1)	2.42 Å	
	O(1)–H(1)$\cdots$Cl(1′)	2.43 Å	
	C(18)–H(18C)$\cdots$O(1′)	2.40 Å	$\sum r_{vdW}$(O,H) 2.60 Å

A 3D supramolecular architecture is formed through additional C–H$\cdots\pi$ (Ar$_{centroid}$) and C–H$\cdots$Cl contacts between dinuclear units in the crystal of **4**·H_2O [symmetry equivalent atoms (*x, 1+y, z*), (*1–x, 0.5+y, 0.5–z*) and (*1+x, y, z*) are given by "a", "b" and "c", respectively].

C(13)–H(13)$_{aryl}\cdots$Ar$_{centroid}$\{C(1a)-C(6a)\}	3.09 Å ($\gamma = 21.6°$)
C(21b)–H(21b)$_{phenyl}\cdots$Cl(1)	2.87 Å
C(3c)–H(3c)$_{aryl}\cdots$Cl(1)	2.94 Å

$[\{2\text{-}(Me_2NCH_2)C_6H_4\}_2PhTe]^+Br^- \cdot H_2O$ ($\mathbf{5} \cdot H_2O$)

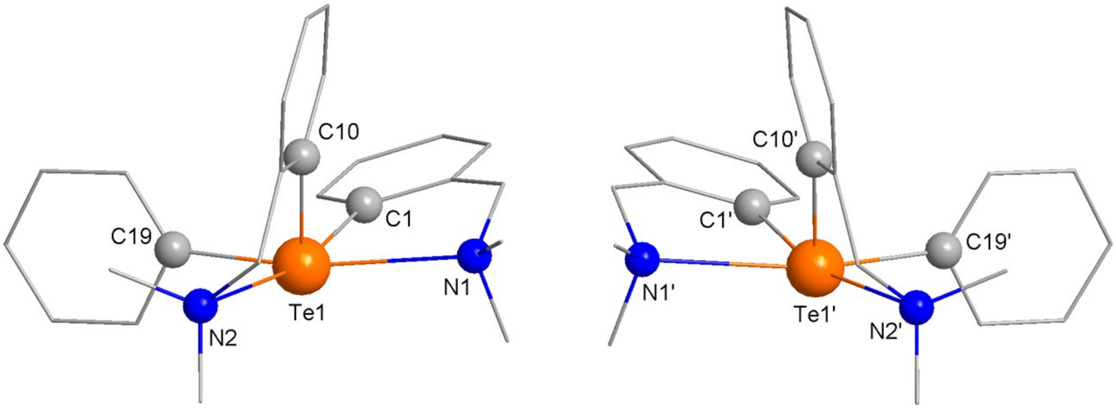

Figure S15. Structures of the $(A_{\mathrm{Te1}})(pS_{\mathrm{N1}},pR_{\mathrm{N2}})$ (or Δ_{Te1}) (*left*) and $(C_{\mathrm{Te1'}})(pR_{\mathrm{N1'}},pS_{\mathrm{N2'}})$ (or Λ_{Te1}) (*right*) cations in the crystal of $\mathbf{5}\cdot H_2O$ (for clarity, hydrogen atoms are not shown) [symmetry equivalent atoms (*–x, –y, 1–z*) are given by "prime"].

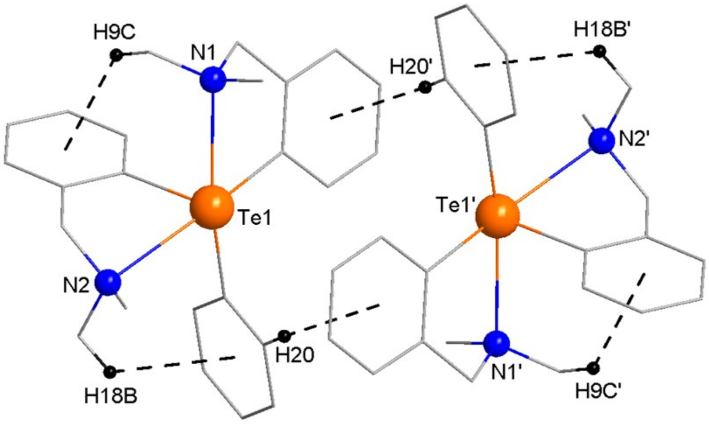

Figure S16. Dinuclear association through C–H$_{\mathrm{phenyl}}\cdots\pi$ (Ar$_{\mathrm{centroid}}$) interactions between $(A_{\mathrm{Te1}})(pS_{\mathrm{N1}},pR_{\mathrm{N2}})$ and $(C_{\mathrm{Te1'}})(pR_{\mathrm{N1'}},pS_{\mathrm{N2'}})$ cations in the crystal of $\mathbf{5}\cdot H_2O$, including additional C–H$_{\mathrm{methyl}}\cdots\pi$ (Ph$_{\mathrm{centroid}}$) and C–H$_{\mathrm{methyl}}\cdots\pi$ (Ar$_{\mathrm{centroid}}$) intra-cation contacts (only hydrogen atoms involved in contacts with aromatic rings are shown) [symmetry equivalent atoms (*–x, –y, 1–z*), are given by "prime"].

- interatomic distances	C(20)–H(20)$_{\mathrm{phenyl}}\cdots$Ar$_{\mathrm{centroid}}$\{C(1′)-C(6′)\}	2.82 Å (γ = 17.7°)
	C(9)–H(9C)$_{\mathrm{methyl}}\cdots$Ar$_{\mathrm{centroid}}$\{C(10)-C(15)\}	3.03 Å (γ = 21.4°)
	C(18)–H(18B)$_{\mathrm{methyl}}\cdots$Ph$_{\mathrm{centroid}}$\{C(19)-C(24)\}	3.05 Å (γ = 16.6°)

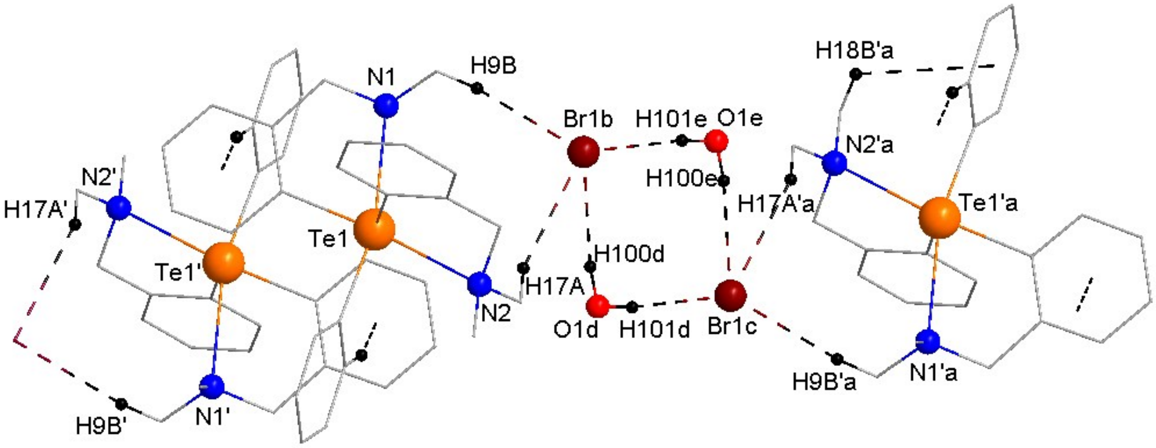

Figure S17. {$Br_2(H_2O)_2$} rectangular units bridging (A_{Te1})(pS_{N1},pR_{N2}) and ($C_{\mathrm{Te1'}}$)($pR_{\mathrm{N1'}}$,$pS_{\mathrm{N2'}}$) cations from different dinuclear associations through C–H···Br contacts in the crystal of **5**·H_2O (only hydrogen atoms involved in contacts with heavier atoms or aromatic rings are shown; for clarity, C–H···π intra-cation contacts are not shown) [symmetry equivalent atoms (*–x, –y, 1–z*), (*–1–x, –y, –z*), (*–1+x, y, z*), (*–x, –y, –z*), (*–x, –y, 1–z*) and (*–1+x, y, –1+z*) are given by “prime”, “prime a”, “b”, “c”, “d” and “e”, respectively].

- interatomic distances	C(17)–H(17A)$_{\mathrm{methyl}}$···Br(1b)	2.94 Å	$\sum r_{\mathrm{vdW}}$(Br,H) 3.15 Å
	C(9)–H(9B)$_{\mathrm{methyl}}$···Br(1b)	3.04 Å	
	O(1e)–H(101e)···Br(1b)	2.54 Å	
	O(1d)–H(100d)···Br(1b)	2.72 Å	

A 3D supramolecular architecture is formed through additional C–H$_{\mathrm{aryl}}$···Br and C–H$_{\mathrm{methylene}}$···Br contacts between dinuclear units in the crystal of **5**·H_2O [symmetry equivalent atoms (*–1+x, y, z*), (*–x, –y, –z*) and (*–0.5+x, 0.5–y, –0.5+z*) are given by “b”, “c” and “f”, respectively].

C(3f)–H(3f)$_{\mathrm{aryl}}$···Br(1b)	2.96 Å	$\sum r_{\mathrm{vdW}}$(Br,H) 3.15 Å
C(13b)–H(13b)$_{\mathrm{aryl}}$···Br(1b)	2.97 Å	
C(16Bc)–H(H16Bc)$_{\mathrm{methylene}}$···Br(1b)	3.14 Å	

$[\{2\text{-}(Me_2NCH_2)C_6H_4\}_2PhTe]^+I^-$ (6)

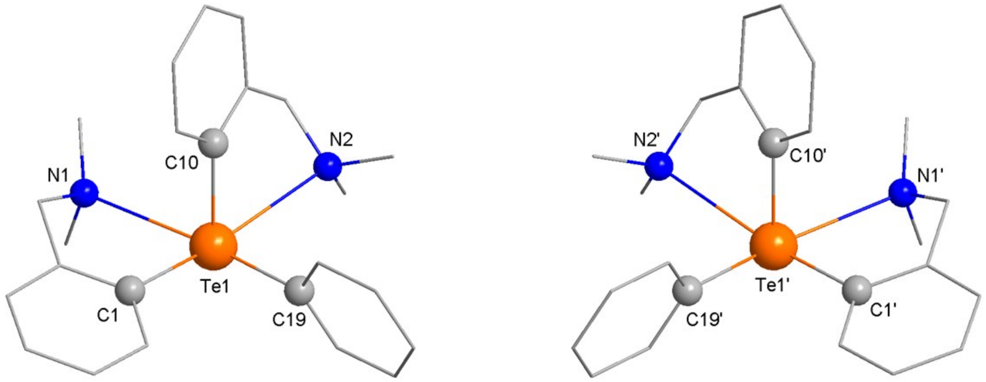

Figure S18. Structures of the $(A_{\mathrm{Te1}})(pS_{\mathrm{N1}},pR_{\mathrm{N2}})$ (or Δ_{Te1}) (*left*) and $(C_{\mathrm{Te1'}})(pR_{\mathrm{N1'}},pS_{\mathrm{N2'}})$ (or Λ_{Te1}) (*right*) cations in the crystal of **6** (for clarity, hydrogen atoms are not shown) [symmetry equivalent atoms (*1–x, 1–y, –z*) are given by "prime"].

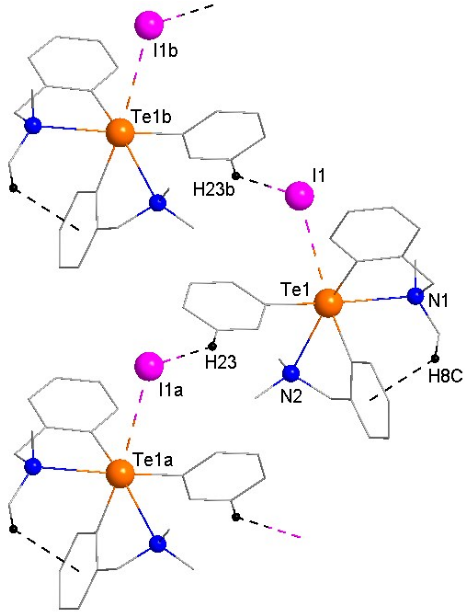

Figure S19. View along *c* axis of a chain of alternating $(A_{\mathrm{Te1}})(pS_{\mathrm{N1}},pR_{\mathrm{N2}})$ cations and iodide anions based on $C–H_{\mathrm{phenyl}}\cdots I$ contacts in the crystal of **6** (only hydrogen atoms involved in contacts with heavier atoms or aromatic rings) [symmetry equivalent atoms (*0.5–x, –0.5+y, 0.5–z*) and (*0.5–x, 0.5+y, 0.5–z*) are given by "a" and "b", respectively].

- interatomic distances	$C(8)–H(8C)_{\mathrm{methyl}}\cdots Ar_{\mathrm{centroid}}\{C(10)\text{-}C(15)\}$	3.00 Å	($\gamma = 20.4°$)
	$C(23)–H(23)_{\mathrm{phenyl}}\cdots I(1a)$	3.14 Å	$\sum r_{\mathrm{vdW}}(I,H)$ 3.35 Å

A 3D supramolecular architecture is formed through additional C–H···I contacts between chains of alternating $(A_{\mathrm{Te1}})(pS_{\mathrm{N1}},pR_{\mathrm{N2}})$ cations and iodide anions and $(C_{\mathrm{Te1'}})(pR_{\mathrm{N1'}},pS_{\mathrm{N2'}})$ cations and iodide anions in the crystal of **6** [symmetry equivalent atoms (*–0.5+x, 1.5–y, –0.5+z*) and (*1–x, 1–y, –z*) are given by "a" and "prime", respectively].

$C(3a)–H(3a)_{\mathrm{aryl}}\cdots I(1)$	3.23 Å	$\sum r_{\mathrm{vdW}}(I,H)$ 3.35 Å
$C(8')–H(8B')_{\mathrm{methyl}}\cdots I(1)$	3.25 Å	
$C(17')–H(17B')_{\mathrm{methyl}}\cdots I(1)$	3.27 Å	

$[\{2\text{-}(Me_2NCH_2)C_6H_4\}_3Te]^+Cl^-\cdot H_2O$ (**7** H_2O)

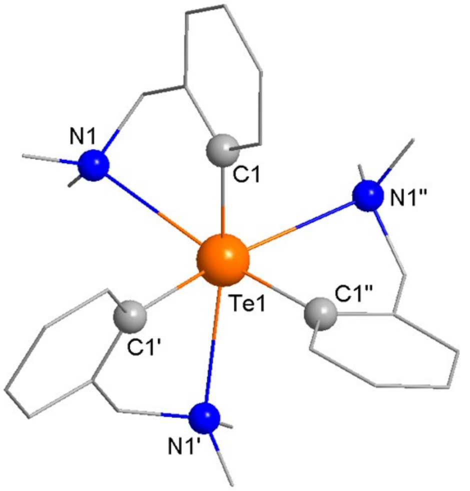

Figure S20. Structure of the (Λ_{Te1})(pS_{N1},$pS_{N1'}$,$pS_{N1''}$) cation (*M* isomer) in the crystal of **7**·H_2O (for clarity, hydrogen atoms are not shown) [symmetry equivalent atoms (*1–y, 2+x–y, z*) and (*–1–x+y, 1–x, z*) are given by "prime" and "double prime", respectively].

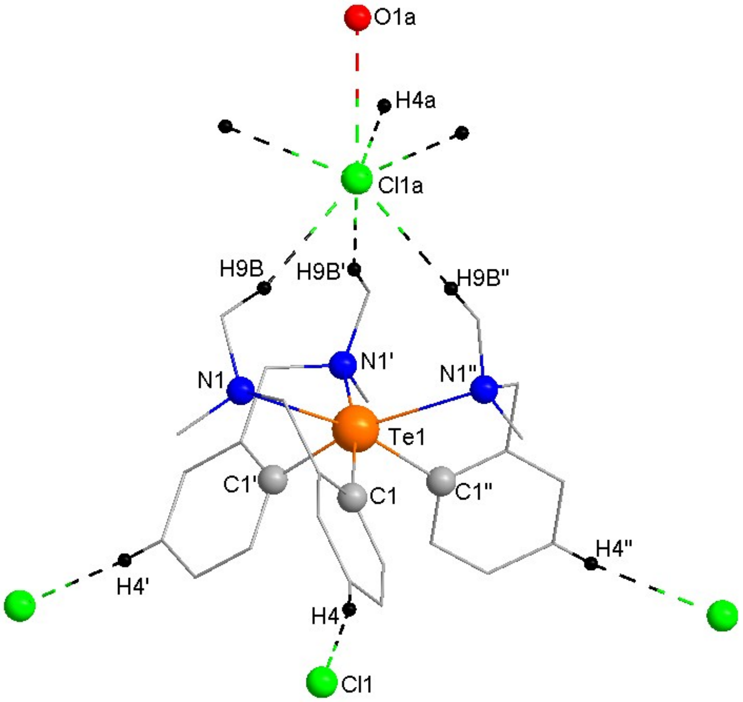

Figure S21. Fragment of the 3D supramolecular architecture built through C–H···Cl and O–H···Cl interactions between (Λ_{Te1})(pS_{N1},$pS_{N1'}$,$pS_{N1''}$) cations, chloride anions and H_2O molecules in the crystal of **7**·H_2O (hydrogen atoms, except those involved in contacts to chloride anion, are omitted for clarity) [symmetry equivalent atoms (*1–y, 2+x–y, z*), (*–1–x+y, 1–x, z*) and (*–0.33+x, 0.33+y,* (*–0.66+z*) are given by "prime", "double prime" and "a", respectively].

C(9)–H(9B)$_{methyl}$···Cl(1a)	2.84 Å	$\sum r_{vdW}$(Cl,H) 3.01 Å
C(4)–H(4)$_{aryl}$···Cl(1)	2.85 Å	
O(1b)···Cl(1b)	3.27 Å	$\sum r_{vdW}$(O,Cl) 3.06 Å

$[\{2\text{-}(Me_2NCH_2)C_6H_4\}_2(OH)Te]^+Cl^-$ (10)

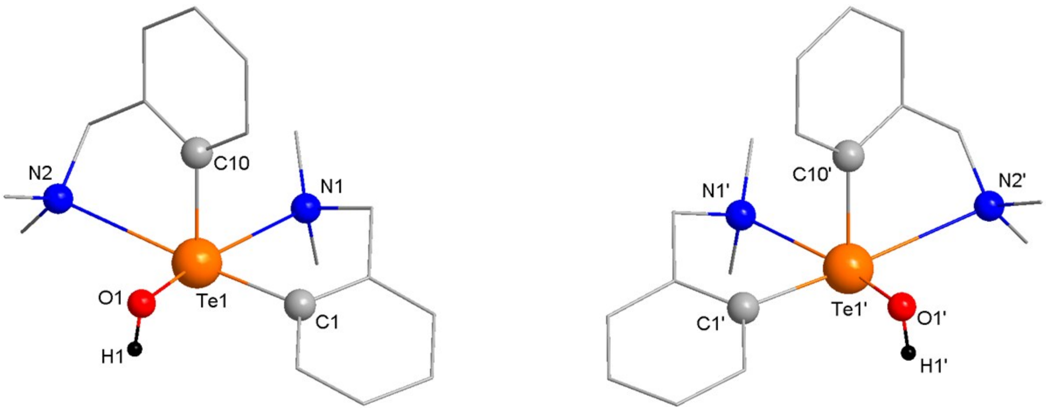

Figure S22. Structures of the $(A_{\text{Te1}})(pR_{\text{N1}},pS_{\text{N2}})$ (or Λ_{Te1}) (*left*) and $(C_{\text{Te1}'})(pS_{\text{N1}'},pR_{\text{N2}'})$ (or Δ_{Te1}) (*right*) cations in the crystal of **10** (for clarity, hydrogen atoms are not shown) [symmetry equivalent atoms (*2–x, 2–y, –z*) are given by "prime"].

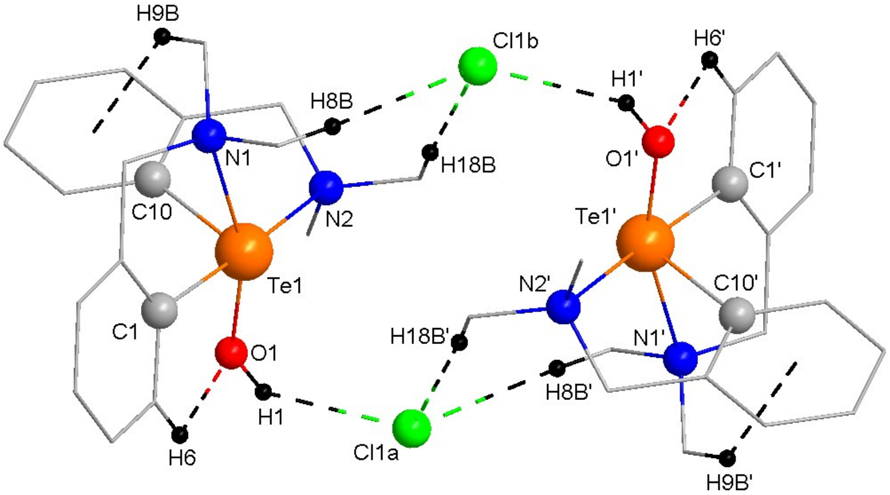

Figure S23. Dinuclear association through interactions between $(A_{\text{Te1}})(pR_{\text{N1}},pS_{\text{N2}})$ and $(C_{\text{Te1}'})(pS_{\text{N1}'},pR_{\text{N2}'})$ cations and chloride anions in the crystal of **10**, including additional $C–H_{\text{methyl}}\cdots\pi$ (Ar_{centroid}) and $C–H_{\text{aryl}}\cdots O$ intra-cation contacts (only hydrogen atoms involved in contacts with heavier atoms or aromatic rings are shown) [symmetry equivalent atoms (*2–x, 2–y, –z*), (*x, 1+y, z*) and (*2–x, 1–y, –z*) are given by "prime", "a" and "b", respectively].

- interatomic distances	$C(9)–H(9B)_{\text{methyl}}\cdots Ar_{\text{centroid}}\{C(10)\text{-}C(15)\}$	3.08 Å (γ = 24.5°)	
-	$O(1')–H(1')\cdots Cl(1b)$	2.43 Å	$\sum r_{\text{vdW}}(Cl,H)$ 3.01 Å
	$C(8)–H(8B)_{\text{methyl}}\cdots Cl(1b)$	2.72 Å	
	$C(18)–H(18B)_{\text{methyl}}\cdots Cl(1b)$	2.76 Å	
	$C(6)–H(6)\cdots O(1)$	2.46 Å	$\sum r_{\text{vdW}}(O,H)$ 2.60 Å

A 3D supramolecular architecture is formed through additional $C–H\cdots\pi$ (Ar_{centroid}) and $C–H\cdots Cl$ contacts between dinuclear units in the crystal of **10** [symmetry equivalent atoms (*2–x, 1–y, –z*), (*1.5–x, –0.5+y, 0.5–z*), (*0.5+x, 1.5–y, 0.5+z*) and (*0.5+x, 1.5–y, –0.5+z*) are given by "b", "c", "d" and "e", respectively].

$C(3c)–H(3c)_{\text{aryl}}\cdots Ar_{\text{centroid}}\{C(10)\text{-}C(15)\}$	2.78 Å (γ = 12.3°)
$C(13d)–H(13d)_{\text{aryl}}\cdots Ar_{\text{centroid}}\{C(1)\text{-}C(6)\}$	2.78 Å (γ = 0.8°)
$C(8b)–H(8Ab)_{\text{methyl}}\cdots Cl(1b)$	2.92 Å
$C(14e)–H(14e)_{\text{aryl}}\cdots Cl(1b)$	2.93 Å

Table S1. Crystal and structural refinement data for compounds **1**, **1**·0.5CH_2Cl_2, **3** and **4**·H_2O.

	1 / CCDC 1912124	**1**·0.5CH_2Cl_2 / CCDC 1912126	**3** / CCDC 1912130	**4**·H_2O / CCDC 1912127
Crystal data				
Empirical formula	$C_{21}H_{22}ClNTe$	$C_{43}H_{46}Cl_4N_2Te_2$	$C_{21}H_{22}INTe$	$C_{24}H_{31}ClN_2OTe$
Formula weight, g/mol	451.45	987.82	542.89	526.56
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a, Å	9.6231(11)	9.0570(7)	23.610(3)	9.0364(7)
b, Å	10.2676(12)	27.374(2)	8.9780(10)	9.9969(8)
c, Å	11.9457(14)	17.6459(14)	20.371(2)	27.008(2)
α, °	70.809(2)	90	90	90
β, °	72.969(2)	92.215(2)	104.827(2)	93.4240(10)
γ, °	69.253(2)	90	90	90
Volume, Å^3	1021.4(2)	4371.6(6)	4174.3(8)	2435.4(3)
Z	2	4	8	4
Density (calculated), g/cm^3	1.468	1.501	1.728	1.436
Absorption coefficient, mm^{-1}	1.589	1.610	2.906	1.348
F(000)	448	1960	2080	1064
Crystal size, mm	0.11 × 0.19 × 0.23	0.19 × 0.22 × 0.30	0.16 × 0.18 × 0.19	0.08 × 0.45× 0.53
Data collection				
Temperature, K	297	297	297	297
Wavelength, Å	0.71073	0.71073	0.71073	0.71073
Theta range for data collection, °	1.8 to 26.0	1.4 to 26.4	0.89 to 25.00	1.5 to 26.4
Dataset	±11; ±12; ±14	±11; ±34; ±22	±28; ±10; ±24	±11; ±12; ±33
Reflections collected / unique data / R(int)	7986 / 3953 / 0.026	34994 / 8937 / 0.050	39109 / 7357 / 0.064	19041 / 4973 / 0.041
Observed Data [$I > 2.0\sigma(I)$]	3594	7191	5846	4543
Refinement				
Absorption correction	Semi-empirical from equivalents			
Refinement method	Full-matrix least-squares on F^2			
Data / restrains / parameters	3953 / 0 / 219	8937 / 0 / 464	7357 / 0 / 437	4973 / 0 / 274
R / $wR2$ / S	0.0326 / 0.0722 / 1.03	0.0606 / 0.1274 / 1.16	0.0697 / 0.1247 / 1.25	0.0333 / 0.0772 / 1.09
Largest diff. peak and hole, e/Å^3	0.72 and −0.26	0.98 and −0.93	0.90 and −1.45	0.64 and −0.52

Table S2. Crystal and structural refinement data for compounds **5**·H_2O, **6**, **7**·H_2O and **10**.

	5·H_2O / CCDC 1912128	**6** / CCDC 1912131	**7**·H_2O / CCDC 1912129	**10** / CCDC 1912125
Crystal data				
Empirical formula	$C_{24}H_{31}BrN_2OTe$	$C_{24}H_{29}IN_2Te$	$C_{27}H_{36}ClN_3OTe$	$C_{18}H_{25}ClN_2OTe$
Formula weight, g/mol	571.02	599.99	581.64	448.45
Crystal system	monoclinic	monoclinic	trigonal	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$R3$	$P2_1/n$
a, Å	9.9565(14)	15.6120(12)	13.3319(14)	11.058(2)
b, Å	17.087(3)	10.4144(8)	13.3319(14)	10.259(2)
c, Å	14.892(2)	16.0155(12)	13.020(3)	17.370(4)
α, °	90	90	90	90
β, °	92.924(3)	110.882(1)	90	100.320(4)
γ, °	90	90	120	90
Volume, Å^3	106.707(2)	2432.9(3)	2004.1(7)	1938.5(7)
Z	4	4	3	4
Density (calculated), g/cm^3	1.563	1.638	1.446	1.536
Absorption coefficient, mm^{-1}	2.889	2.503	1.237	1.678
F(000)	1136	1168	888	896
Crystal size, mm	0.26 × 0.32 × 0.34	0.24 × 0.25 × 0.30	0.19 × 0.20 × 0.21	0.22 × 0.33 × 0.38
Data collection				
Temperature, K	297	297	297	294
Wavelength, Å	0.71073	0.71073	0.71073	0.71073
Theta range for data collection, °	2.2 to 26.4	2.3 to 26.4	2.4 to 26.4	2.3 to 25.0
Dataset	±12; ±21; -18/17	±19; ±13; −19/20	±16; ±16; ±16	±13; ±12; ±20
Reflections collected / unique data / R(int)	19115 / 4958 / 0.041	19053 / 4959 / 0.032	7026 / 1822 / 0.052	17848 / 3394 / 0.063
Observed Data [$I > 2.0\sigma(I)$]	4377	4588	1803	2890
Refinement				
Absorption correction	Semi-empirical from equivalents			
Refinement method	Full-matrix least-squares on F^2			
Data / restrains / parameters	4958 / 3 / 274	4959 / 0 / 257	1822 / 1 / 117	3394 / 0 / 212
R / $wR2$ / S	0.0400 / 0.0846 / 1.13	0.0407 / 0.0839 / 1.21	0.0296 / 0.0263 / 1.02	0.0366 / 0.0737 / 1.05
Flack x	-	-	−0.011(19)	-
Largest diff. peak and hole, e/Å^3	0.76 and −0.76	0.81 and −0.74	0.94 and −0.24	0.49 and -0.47