Substituent-Controlled Tailoring of Chalcogen-Bonded Supramolecular Nanoribbons in the Solid State

Nicolas Biot, Deborah Romito, and Davide Bonifazi*

ABSTRACT: In this work, we design and synthesize supramolecular 2,5-substituted chalcogenazolo[5,4-β]pyridine (CGP) synthons arranging in supramolecular ribbons at the solid state. A careful choice of the combination of substituents at the 2- and 5-positions on the CGP scaffold is outlined to accomplish supramolecular materials by means of multiple hybrid interactions, comprising both chalcogen and hydrogen bonds. Depending on the steric and electronic properties of the substituents, different solid-state arrangements have been achieved. Among the different moieties on the 5-position, an oxazole unit has been incorporated on the Se- and Te-congeners by Pd-catalyzed cross-coupling reaction and a supramolecular ribbon-like organization was consistently obtained at the solid state.

INTRODUCTION

In recent years, crystal engineering has soared interest in the scientific community, given its valuable implications in the rational design of functional materials. Several studies have focused on the use of supramolecular bonds, selectively involving recognition motifs to generate stable and predictable multidimensional networks in the solid state. Among the several noncovalent interactions, hydrogen bonds embody the main interaction occurring in biological systems, as well as being used for many applications in chemistry and materials science. However, over the past decades, there has been a flourishing interest for a class of exotic noncovalent interactions, namely, Secondary Bonding Interactions (SBIs), as attractive alternatives to the ubiquitous hydrogen bond in crystal engineering. SBIs’ nature relies on electrostatic contributions, as well as on orbital mixing described as n(Y)→σ*(E-X) donation (X-E···Y), which involves non-bonding electrons of the electron-donating atom Y and the empty antibonding σ*-E located on the E atom. When the central polarizable E atom belongs to Group VI of the periodic table, the term chalcogen bonding (EB, known also as ChB) is used to describe the interaction between a positively polarized chalcogen atom and a Lewis base. Despite recent developments in catalysis and sensing, EB interactions have been mainly exploited in crystal engineering, providing a distinctive series of persistent recognition motifs. The structure of the most part of these chalcogen-bonding synthons builds on a heterocyclic scaffold, in which the chalcogen bond donors and acceptors are proximal to each other, thus effectively developing macrocyclic and wire-like supramolecular architectures. Previous work done in our group with 2-substituted benzo-1,3-chalcogenazoles described the formation of polymeric structures achieved through single EB interactions. When using the chalcogenazolo[5,4-β]pyridine (CGP) module, frontal double chalcogen bonds are obtained in the solid state with high recognition fidelity when the Te chalcogen is used. Notably, changing the derivatization in the 2-position of the CGP ring has allowed the complexity of the molecular assembly to be expanded, engineering organic solids through...
the co-crystallization of heteromolecular supramolecular polymers, held by concurring chalcogen- and halogen-bonding interactions. Building on these results, in this work, we pursue the idea of expanding the functionalization space of the CGP module in the 5-position. This would allow face-to-face dimer association to be disrupted and originate new recognition modes in the solid state (see Figure 1).

**Design of 2- and 5-Substituted CGP Derivatives.** We conjectured that, depending on the electronic and steric properties of the substituents in the 2- and 5-positions, one could disrupt the typical doubly chalcogen-bonded recognition of a CGP-based derivative (recognition mode A, Figure 1) and force the module to associate in a different fashion. For instance, if the substituent in the 5-position (orange) sterically clashes with that in the 2-position (green) in the frontal arrangement, one could envisage that a head-to-tail recognition mode is favored (e.g., B and C modes displayed in Figure 1). In this arrangement, an EB is established between the N atom of the chalcogenazole ring (Nₐ) and the chalcogen atom of a neighboring CGP moiety. If no homo-repulsions are present between the substituents in the 2-position (green), a noncovalent ribbon-like organization, held together by a combination of frontal hydrogen- and chalcogen-bonding interactions, is expected to develop (mode B, Figure 1). Finally, if all substituents would undergo homo- and hetero-repulsions in the frontal arrangements, then the only possibility would be for the motif to assemble into nonplanar chalcogen-bonded wire-like assemblies (mode C, Figure 1), as previously observed by us. Aiming at developing synthetically accessible modules with high recognition fidelity, we have focused on the preparation of Te-containing derivatives. Cl, I, and Me groups were chosen as substituents for the 5-position, whereas phenyl, thiophenyl (Th), and CF₃ moieties for the 2-position. To describe the different combinations of substituents in the 2- and 5-positions, the molecules are labeled as Y-E-R, where Y stands for the substituent in the 5-position (schematized as an orange sphere, Figure 1), E is the chalcogen atom of interest, and R is the moiety in the 2-position (schematized as a green sphere, Figure 1), respectively.

In our molecular engineering plan, the CGP modules bearing the CF₃ moiety in the 2-position and the bulkiest (Me) and electronegative (Cl) groups in the 5-position (e.g., Me-Te-CF₃ and Cl-Te-CF₃) are expected to assemble in a head-to-tail fashion. Similarly, oxazole-bearing Ox-E-CF₃ is expected to arrange head-to-tail in ribbon-like architectures, with the oxazole ring further strengthening the association through weak H-bonding interactions. On the other hand, when a sizable group is added in the 2-position, the formation of wire-like assemblies is expected (e.g., Cl-Te-R and I-Te-Ph). Given that repulsive forces originating from the close proximity of the substituents in the self-assembled structure could arise from either steric or electrostatic contributions, electrostatic surface potential (ESP) maps were computed to further understand the contribution of the electrostatic component (see Supporting Information (SI), Table S1 for the calculated Vₛₘₐₓ values).

### RESULTS AND DISCUSSION

**Synthesis.** The synthesis started with the selective bromination of the commercially available amines 1Me and 1Cl using N-bromo succinimide (NBS) in MeCN, which provided compounds 2Me and 2Cl, respectively, in good and excellent yields. Brominated amines 2Me and 2Cl were treated with 1 equiv of n-BuLi, followed by the addition of 1 equiv of...
trialkyl magnesate (freshly prepared by mixing i-PrMgCl with 2 equiv of n-BuLi). Subsequent addition of the relevant freshly grounded elemental chalcogen powder to the reaction mixture led to the corresponding bischalcogenides \(3_X\) in significantly improved yields (28−55%) when compared to synthetic protocols previously implemented by our group.

The synthesis of derivatives \(4_X\) was completed by the reductive cleavage of the dichalcogenide bond using NaBH\(_4\) and MeOH in THF, followed by addition of MeI. To insert the CF\(_3\) moiety in the 2-position, a one-pot amidation/dehydrative cyclization reaction was performed on \(4_X\) using Tf\(_2\)O in a 1:1 mixture of CH\(_2\)Cl\(_2\) and pyridine, followed by the addition of POCl\(_3\) in a 1:1 DIPEA/dioxane solution under refluxing conditions to give X-E-CF\(_3\). In parallel, Te-bearing amine \(4_cl\) was converted into amides \(5_{cl\_te}\) upon reaction with the relevant acyl chloride which, followed by cyclization in the presence of POCl\(_3\) in DIPEA and dioxane, afforded Cl-Te-R in excellent yields. Given the proved chemical compatibility of the CGP moiety with Pd-catalyzed cross-coupling conditions, a Negishi cross-coupling reaction was attempted to prepare Ox-Te-Ph starting from chloro-derivative Cl-Te-Ph. Nevertheless, no conversion was observed.

Thus, we moved our attention to the iodo-bearing congeners as electrophilic substrates. As a result, cyclized products bearing chlorine in the 5-position, i.e., CI-E-CF\(_3\) and CI-Te-Ph, were transformed into iodo-containing I-E-CF\(_3\) and I-Te-Ph using NaI in the presence of AcCl in MeCN at 80 °C under microwave irradiation. Finally, reaction between the iodinated derivatives and oxazol-2-ylzinc(II) chloride using [Pd(PPh\(_3\))] in THF at reflux afforded targeted molecules Ox-E-R in good yields (Scheme 1). All compounds were fully characterized by \(^1\)H, \(^{19}\)F, and \(^{13}\)C NMR spectroscopy, IR, mp, and HR-mass spectrometry (see SI).

**Solid-State Self-Assembly.** The association properties of the 2,5-functionalized CGP derivatives in the solid state were probed by X-ray analysis of single crystals, generally obtained

---

**Scheme 1. Synthetic Pathway to 2,5-Functionalized CGP Derivatives**

![Scheme 1](https://dx.doi.org/10.1021/acs.cgd.0c01318)

Reagents and conditions: (a) NBS, MeCN, r.t., 5 min; (b) 1. n-BuLi, THF, 0 °C, 10 min; 2. i-PrBu, MgLi-LiCl, 0 °C, 1 h; 3. E, r.t., overnight; 4. Se: K\(_2\)Fe(CN)\(_6\), H\(_2\)O, r.t., 10 min; Te: NH\(_4\)Cl, H\(_2\)O, air, r.t., 2 h; (c) 1. NaBH\(_4\), MeOH, THF, r.t., 1 h; 2. Mel, r.t., 1.5 h; (d) 1. (CF\(_3\)CO\(_2\))\(_2\)O, CH\(_2\)Cl\(_2\), pyridine, 0 °C to r.t., overnight; 2. POCl\(_3\), DIPEA, 1,4-dioxane, reflux, overnight; (e) acyl chloride, CH\(_2\)Cl\(_2\), pyridine, 0 °C to r.t., overnight; (f) POCl\(_3\), DIPEA, 1,4-dioxane, reflux, overnight; (g) AcCl, NaI, MeCN, 80 °C, MW, 12 h; (h) oxazol-2-ylzinc(II) chloride, [Pd(PPh\(_3\))] in THF, reflux, 2 h.
by slow evaporation of a CHCl₃ solution. Governed by fluorophilic domains established by the CF₃ moiety in the 2-position, crystals of Me-Te-CF₃ and Cl-E-CF₃ are isomorphs, despite bearing either a Me or Cl atom in the 5-position, either Se or Te atoms. Te-congeners Me-Te-CF₃ (Figure 2a) and Cl-Te-CF₃ (Figure 2e) develop in a ribbon-like arrangement, in which each molecule is involved in frontal interactions comprising a chalcogen bond ($d_{N_{C} \cdots Te} = 3.423$ and 3.406 Å for Me-Te-CF₃ and Cl-Te-CF₃, respectively) and a hydrogen bond, with the latter established between the pyridyl H and N atoms ($d_{N_{p} \cdots C} = 3.420$ and 3.385 Å, respectively, for Me-Te-CF₃ and Cl-Te-CF₃). Surprisingly, the Se-based congener, Cl-Se-CF₃ (Figure 2c), arranges in an analogue ribbon-like orientation (Figure 2c), though held together only by hydrogen-bonding interactions ($d_{N_{p} \cdots C} = 3.351$ Å). Additional π−π stacking interactions, governing the columnar stacking arrangement in a head-to-tail fashion, are also observed ($d_{\pi-\pi} = 3.529$ Å), with the longest distance reported for Me-Te-CF₃. Considering the ESP map of the two different moieties in the S-position (i.e., depicting the Me group mostly positive and Cl atom mostly negative), one can easily conjecture that the formation of assembly A for Me-Te-CF₃ is hampered by steric repulsion in the case of CF₃ and Me, whereas, in Cl-Te-CF₃, CF₃ and Cl repel each other through a strong electrostatic component.

Moving to the crystal structure of iodo-derivative I-Te-CF₃, a different molecular packing could be observed. Interestingly, doubly chalcogen-bonded, distorted noncovalent dimers are observed ($d_{N_{C} \cdots Te} = 3.217$ Å). Given the low electronegativity and high polarizability of the I atom, the solid-state arrangement suggests the presence of a weaker repulsion between the CF₃ and I atoms, compared to that between CF₃ and Cl (Figure 3a). Moreover, each dimer associates through double hydrogen bonds involving the Nₜ atom ($d_{N_{p} \cdots C} = 3.486$ Å), hence generating a kinked ribbon at the solid state (Figure 3b). π−π stacking interactions are also observed ($d_{\pi-\pi} = 3.824$ Å) and each column interconnected by multiple halogen bonds ($d_{I\cdots I} = 3.482$ Å). In this arrangement, each I atom acts simultaneously as both halogen-bonding acceptor and donor (Figure 3c). As previously observed for compound Cl-Se-CF₃, also I-Se-CF₃ crystallizes through the formation of ribbon-like structures with no detectable chalcogen-nitrogen contacts. In these crystals, the monomers organize through hydrogen-bonding interaction ($d_{N_{p} \cdots C} = 3.418$ Å), which are considerably longer than those observed for Cl-Se-CF₃ (Figure 3d). Notably, I-Se-CF₃ forms columns through π−π stacking interactions (estimated $d_{\pi-\pi} = 3.489$ Å), having the CF₃ moieties segregated in fluorinated domains ($d_{F\cdots F} = 2.573$ and 2.933 Å; Figure 3e). The functionalization of the 2-position with the thiophenyl unit for Cl-Te-Th and the phenyl ring for Cl-Te-

Figure 2. X-ray structures and their respective ESP maps of (a) Me-Te-CF₃, (c) Cl-Se-CF₃, and (e) Cl-Te-CF₃; π−π stacking arrangements of (b) Me-Te-CF₃, (d) Cl-Se-CF₃, and (f) Cl-Te-CF₃. Space group: $P2_1/m$. Crystallization solvent: CHCl₃.
Ph and I-Te-Ph leads to the growth of wire-like supramolecular structures, held together by single EB between the N\textsubscript{c} atom and the Te atom of each neighboring molecule. Notably, the asymmetric unit of compound Cl-Te-Th includes two molecules, building a wire-like supramolecular assembly through single EB interactions involving the tellurazole N atom ($d_{N\textsubscript{c}-Te} = 3.385$ Å; Figure 4a). A similar solid-state organization, as that obtained for Cl-Te-Th, was observed for Cl-Te-Pb. In this case, both Te $\sigma$-holes are involved in EB interactions (Figure 4b). Specifically, the $\sigma$-hole($\alpha$) engages with the tellurazole N\textsubscript{c} atom, developing the wire-like arrangement ($d_{N\textsubscript{c}-Te} = 3.464$ Å; Figure 4d), whereas the $\sigma$-hole($\beta$) bridges the neighboring supramolecular wires through the interaction with the N\textsubscript{p} atom ($d_{N\textsubscript{p}-Te} = 3.431$ Å). Furthermore, the molecules are held together through $\pi-\pi$ stacking interactions in a quasi-parallel fashion (estimated $d_{\pi-\pi} = 3.460$ Å), with halogen–halogen interactions connecting the columnar architectures ($d_{Cl-CF} = 3.244$ Å; Figure 4c). In the case of iodo-derivative I-Te-Pb, the asymmetric unit contains two molecules, each interacting with a nearby module through single EB with the N\textsubscript{c} atom ($d_{N\textsubscript{c}-Te} = 3.464$ and 3.582 Å). The resulting wire-like organization is further strengthened by weak hydrogen contacts established between the N\textsubscript{p} atom and one of the H atoms of the phenyl ring ($d_{N\textsubscript{p}-H} = 3.237$ and 3.321 Å; Figure 4e). In contrast to chlorinated analogue Cl-Te-Pb, $\pi-\pi$ stacking interactions govern the formation of columnar arrangements in a quasi-parallel head-to-tail fashion (estimated $d_{\pi-\pi} = 3.542$ Å), with $\pi-\pi$ interactions ($\sigma^*-\pi$, $d_{\pi-\pi} = 3.505$ Å) bridging the columns (Figure 4f).

Building on these observations, one can notice that wire-like structures are consistently attained over ribbon and dimeric arrangements with S-functionalized CGP modules bearing a phenyl moiety in the 2-position. Remarkably, a shortening of the N\textsubscript{c}−Te distance can be observed when passing from phenyl-substituted Cl-Te-Pb and I-Te-Pb to Cl-Te-Th.

Aiming at validating the occurrence of recognition motifs with multiple intermolecular interactions in the solid state, several crystallization attempts for oxazole derivatives Ox-Te-Pb and Ox-E-CF\textsubscript{3} have been performed. However, only the CF\textsubscript{3}-containing compounds provided single crystals suitable for X-ray diffraction analysis. Notably, Te-congener Ox-Se-CF\textsubscript{3} develops HB/EB ribbons in the solid state. These structures differentiate from those described so far because the O atom of the oxazole and the N atom of the pyridyl moiety both engage in two hydrogen bonds with the H atoms in positions 6 and 7 of a neighboring molecule ($d_{O-H} = 3.211$ Å and $d_{N\textsubscript{p}-H} = 3.423$ Å, respectively). A frontal chalcogen bond is also established between the N\textsubscript{c} and Te atoms of two adjacent molecules ($d_{N\textsubscript{c}-Te} = 3.355$ Å; Figure 5a). Considering that the length of this EB is shorter ($d_{N\textsubscript{c}-Te} = 3.355$ Å) than those found in the crystal structures of Me-Te-CF\textsubscript{3} and Cl-Te-CF\textsubscript{3} ($d_{N\textsubscript{c}-Te} = 3.423$ and 3.406 Å, respectively), it is suggested that two HB interactions synergistically strengthen the association between the two molecular modules. Supplementary $\pi-\pi$ stacking interactions can be discerned in the molecular packing ($d_{\pi-\pi} = 3.392$ Å; Figure 5b), with each molecular module arranged in an antiparallel fashion. An analogue supramolecular organization is observed for Se-based congener Ox-Se-CF\textsubscript{3}, having the O atom involved in a hydrogen bond,
as well as the $N_p$ atom, with the H atoms in 6- and 7-positions of the facing molecular neighbor ($d_{O-C} = 3.201 \text{ Å}$, $d_{N_p-C} = 3.418 \text{ Å}$). This governs the arrangement of the synthons in ribbons at the solid state (Figure 5c). Similarly to Cl-Se-CF$_3$ and I-Se-CF$_3$, no chalcogen bond could be observed for Ox-Se-CF$_3$, given that the Se···N distance was longer than the sum of their van der Waals radii ($d_{N_c-Se} = 3.514 \text{ Å} > 3.45 \text{ Å}$). In addition, the crystal packing develops through antiparallel $\pi-\pi$ stacking ($d_{\pi-\pi} = 3.369 \text{ Å}$; Figure 5d).

**CONCLUSIONS**

In this paper, we have expanded the recognition space of the CGP moiety in the solid state. By combining the substituents in positions 2 (phenyl, thiophenyl, and CF$_3$ moieties) and 5 (Me group, Cl and I atoms), a large variety of supramolecular assemblies in the solid state could be obtained by modulating the substituents’ steric and electronic properties. Aiming at developing a recognition pattern based on multiple HB and simultaneous single EB interactions, oxazolyl-bearing CGP molecules Ox-Te-CF$_3$ and Ox-Se-CF$_3$ have been prepared, with the latter used as reference compound to study the role of the chosen chalcogen atom in the new recognition systems. As expected, the choice of a small moiety as CF$_3$ in the 2-position, combined with Me, Cl, and oxazole substituents in the 5-position, governed the formation of supramolecular head-to-tail HB/EB ribbons. Replacing Cl with an I atom in the 5-position in Te-congener I-Te-CF$_3$ led to the formation of distorted EB dimers, arranged into a kinked ribbon in the solid state. Furthermore, derivatives bearing sterically demanding phenyl and thiophenyl groups showed the typical wiring organization. These results could open the road toward the engineering of a large variety of materials marked by tunable molecular arrangements, as well as depicting heteromolecular recognition systems involving HB and EB interactions. The encoding of concomitant weak interactions at the solid state could allow the design of multiresponsive materials for applications in optoelectronics and sensing.
Figure 5. X-ray structures and their ESP maps of (a) Ox-Te-CF$_3$ and (c) Ox-Se-CF$_3$, stick representation of the $\pi-\pi$ stacking of (b) Ox-Te-CF$_3$ and (d) Ox-Se-CF$_3$. H atoms are omitted for clarity. Space groups: Pnma for Ox-Te-CF$_3$, $P2_1/c$ for Ox-Se-CF$_3$. Crystallization solvents: EtOH for Ox-Te-CF$_3$, C$_6$H$_6$ for Ox-Se-CF$_3$.
(9) Lehnh, J. M. Towards complex matter: supramolecular chemistry and self-organization. *European Review* 2009, 17, 263–280.

(10) Stupp, S. I.; Palmer, L. C. Supramolecular chemistry and self-assembly in organic materials design. *Chem. Mater.* 2014, 26, 507–518.

(11) Sarkhel, S.; Desiraju, G. R. N-H···O, O-H···O, and C-H···O hydrogen bonds in protein–ligand complexes: Strong and weak interactions in molecular recognition. *Proteins: Structure, Function, Genet.* 2004, 54, 247–259.

(12) Sivakova, S.; Rowan, S. J. Nucleobases as supramolecular motifs. *Chem. Soc. Rev.* 2005, 34, 9–21.

(13) Wilson, A. J. Non-covalent polymer assembly using arrays of hydrogen-bonds. *Soft Matter* 2007, 3, 409–425.

(14) Medhekar, N. V.; Ramasubramaniam, A.; Rouff, R. S.; Shenoy, V. B. Hydrogen bond networks in graphene oxide composite paper: structure and mechanical properties. *ACS Nano* 2010, 4, 2300–2306.

(15) Herbst, S.; Soberats, K.; Leowanawat, P.; Lehmann, M.; Wüthrich, F. A Columnar Liquid-Crystal Phase Formed by Hydrogen-Bonded Perylene Bisimide J-Aggregates. *Angew. Chem.* 2017, 129, 2194–2197.

(16) Du, X.; Lu, X.; Zhao, J.; Zhang, Y.; Li, X.; Lin, H.; Zheng, C.; Tao, S. Hydrogen bond induced green solvent processed high performance ternary organic solar cells with good tolerance on film thickness and blend ratios. *Adv. Funct. Mater.* 2019, 29, 1902078.

(17) Alcock, N. W. In *Advances in Inorganic Chemistry and Radiochemistry*, Vol. 15; Elsevier, 1972; pp 1–58.

(18) Politzer, P.; Murray, J. S.; Clark, T. Halogen bonding and other σ-hole interactions: a perspective. *Phys. Chem. Chem. Phys.* 2013, 15, 11178–11189.

(19) Cozzolino, A. F.; Elder, P. J. W.; Vargas-Baca, I. A survey of tellurium-centered secondary-bonding supramolecular synths. *Coord. Chem. Rev.* 2011, 255, 1426–1438.

(20) Werz, D. B.; Geiter, R.; Rominger, F. Nanotube formation favored by chalcogen–halogen bonding interactions in supramolecular polymers for crystal engineering. *Chem. Soc. Rev.* 2010, 39, 1324–1329.

(21) Pascoe, D. J.; Ling, K. B.; Cockroft, S. L. The origin of halogen-bonding interactions. *J. Am. Chem. Soc.* 2002, 124, 10638–10639.

(22) Akeroy, C. B.; Bryce, D. L.; Desiraju, G. R.; Frontera, A.; Legon, A. C.; Nicotra, F.; Rissanen, K.; Scheiner, S.; Terraneo, G.; Metrangolo, P.; Resnati, G. Definition of the chalcogen bond (IUPAC recommendations). *Coord. Chem. Rev.* 2005, 258, 1271–1334.

(23) Wonner, P.; Vogel, L.; Däser, M.; Gomes, L.; Kniep, F.; Mållic, B.; Werz, D. B.; Huber, S. M. Carbon–Halogen Bond Activation by Selenium-Based Chalcogen Bonding. *Angew. Chem., Int. Ed.* 2017, 56, 12009–12012.

(24) Benz, S.; Besnard, C.; Matile, S. Chalcogen Bonding Catalysis: From Neutral to Cationic Benzoselenadiazole Scaffolds. *Helv. Chim. Acta* 2018, 101, e1800075.

(25) Vogel, L.; Wonner, P.; Huber, S. M. Chalcogen Bonding: An overview. *Angew. Chem., Int. Ed.* 2019, 58, 1880–1891.

(26) Wonner, P.; Dreger, A.; Vogel, L.; Engelose, E.; Huber, S. M. Chalcogen Bonding Catalysis of a Nitro-Michael Reaction. *Angew. Chem., Int. Ed.* 2019, 58, 16923–16927.

(27) Macchione, M.; Goujon, A.; Strakova, K.; Humeniuk, H. V.; Li, G.; Takhorsheid, E.; Sakai, N.; Matile, S. A Chalcogen-Bonding Catalysis: Exploring the recognition properties of sulfur. *Chem. - Eur. J.* 2019, 25, 323–333.

(28) Kremer, A.; Aurischio, C.; De Leo, F.; Ventura, B.; Wouters, J.; Armario, N.; Barbieri, A.; Bonifazi, D. Walking down the halogenergic chalcogen bonding 2S–2N squares versus competing interactions: Exploring the recognition properties of sulfur. *Chem. - Eur. J.* 2015, 21, 15377–15387.

(29) Kremer, A.; Fermi, A.; Biot, N.; Wouters, J.; Bonifazi, D. Supramolecular Wiring of Benzo-1,3-chalcogenazoles through Programmed Chalcogen Bonding Interactions. *Chem. - Eur. J.* 2016, 22, 5665–5675.

(30) Biot, N.; Bonifazi, D. Programming Recognition Arrays through Double Chalcogen-Bonding Interactions. *Chem. - Eur. J.* 2018, 24, 5439–5443.

(31) Biot, N.; Bonifazi, D. Concurring Chalcogen- and halogen-bonding interactions in supramolecular polymers for crystal engineering applications. *Chem. - Eur. J.* 2020, 26, 2904–2913.

(32) Inoue, A.; Kitagawa, K.; Shimokubo, H.; Oshima, K. Selective Halogen–Magnesium Exchange Reaction via Organomagnesium Ate Complex. *J. Org. Chem.* 2001, 66, 4333–4339.

(33) Romito, B.; Diet, N.; Babdrud, F.; Bonifazi, D. Non-covalent bridging of thiophenenes through chalcogen bonding: a new approach. *Chem. - Eur. J.* 2020, 26, 6732–6738.

(34) Bissemberg, A. C.; Banwell, M. G. Microwave-assisted trans-halogenation reactions of various chloro-, bromo-, trifluoromethane-sulfoniloxy- and nonafluorobutanesulfonyloxy-substituted quinolines, isoquinolines, and pyridines leading to the corresponding iodinated heterocycles. *J. Org. Chem.* 2009, 74, 4893–4895.