

Topochemical polymerization of a diacetylene in a chalcogen-bonded (ChB) assembly

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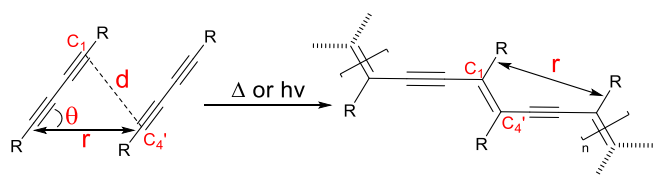
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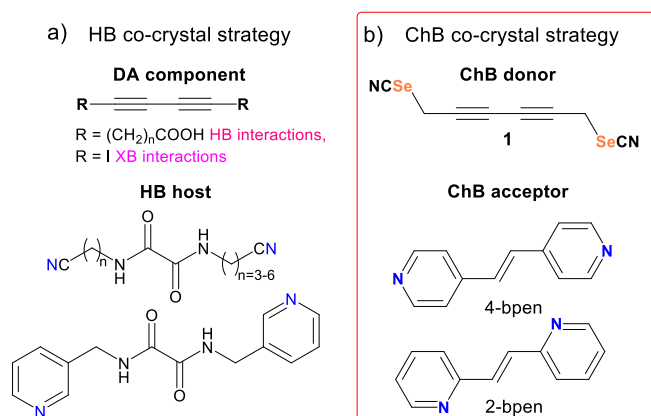
Abstract: The successful topochemical polymerization of bis(selenocyanatomethyl)butadiyne **1** is achieved upon association in a 1:1 co-crystal with 1,2-bis(2-pyridyl)ethylene (2-bpen) through strong and linear (NC)–Se \cdots N_{py} chalcogen bonding (ChB) interactions, allowing for an appropriate parallel alignment of the diacetylene moieties toward the solid state reaction. Co-crystal **1**•(2-bpen) undergoes polymerization upon heating at 100°C. The reaction progress was followed by IR, DSC and PXRD. An enhancement of the polymer conductivity by 8 orders of magnitude is observed upon iodine doping. Strikingly, the course of polymerization is accompanied with sublimation of the ChB acceptor molecules 2-bpen, providing the polymer in a pure form with full recovery of the co-former, at variance with the usual hydrogen bonded co-crystal strategies toward polydiacetylenes.

Crystal engineering strategies favoring topochemical reactions between precisely pre-organized molecules in the solid-state lead to advanced molecular materials that otherwise wouldn't be accessible through classical chemistry in solution. One example of this successful supramolecular approach is polydiacetylene (PDA), a one-dimensional, highly polarizable π -conjugated polymer containing C=C and C \equiv C in an alternating fashion.^[1] Multi-photon absorption in PDAs^[2,3] makes them excellent candidates toward non-linear optical properties^[4-7] but also drug delivery^[8] or semiconducting materials^[9-11]. The topochemical syntheses of PDA require an ordered solid-state arrangement of diacetylene (DA) monomers in crystals that meets specific criteria (Scheme 1), such as a parallel arrangement of DA monomers, a separation (r) of 4.9-5 Å commensurate with the repeat distance in the final polymer, and a tilt angle (θ) of $\sim 45^\circ$ needed to reach a distance (d) of 3.5 Å between C1 of one monomer and the C4' of neighboring monomer (Scheme 1).^[12,13]



Scheme 1. Favorable alignment of acetylenes for 1,4-polymerization with values $r = 4.9\text{--}5.0$ Å, $\theta = 45^\circ$ and $d = 3.5$ Å.

Two main supramolecular strategies have been developed to date to align DAs into such a reactive orientation: (i) a single-component strategy with DA scaffolds containing self-assembling supramolecular synthons, for example carbamate-based hydrogen bonding synthons,^[14] (ii) a multi-component strategy based on co-crystal formation.^[15] The latter has proven to be particularly efficient and reliable to align DAs in the solid-state while meeting the requisites for topochemical polymerization.^[16,17] It is based on a host structure held together by strong hydrogen bonding (HB) synthons such as diamides, interacting through secondary interactions with the DA molecule (Scheme 2a).^[18] Along these lines, Goroff *et al.* prepared poly(diiododiacetylene), through topochemical polymerization of co-crystals between diiodobutadiyne and oxalamides (Scheme 2a).^[19] In such systems, the 4.9 Å rule was satisfied through the strong HB motifs of the oxalamide hosts while the diiodobutadiyne was anchored to this HB matrices through weaker I \cdots N halogen bonds (XB).^[20,21] In all cases, the hydrogen-bonded host structure stays embedded into the final PDA polymer, which is therefore not obtained as a pure form.



Scheme 2. (a) HB co-crystal strategy with examples of DA molecules and hydrogen bonded hosts. (b) ChB co-crystal strategy with ChB donor **1** and pyridine-based ditopic ChB acceptors.

Besides hydrogen bonding, σ -hole interactions have recently garnered great attention as a useful tool in crystal engineering and we wondered if DA polymerization could be favored in co-crystals exclusively based on such weaker interactions, without help of any HB matrices. Halogen bond (XB)^[22] is one of well recognized σ -hole interactions for its strength, directionality and most importantly predictability. However, examples of solid-state reactivity controlled by XB still remain scarce.^[23,24] Similarly, chalcogen bond (ChB) has been defined as an attractive interaction between electropositive area of a chalcogen atom and a Lewis-base.^[25] In contrast to monovalent halogens, a divalent chalcogen atom bears two σ -holes roughly in the prolongation of each covalent bond, limiting the predictability of ChB interactions and its extensive use in crystal engineering,^[26] catalysis^[27] or anion recognition.^[28] To circumvent this problem, a chalcogen atom can be disymmetrized with only one EWG to force a stronger electron depletion along one single direction. Along these lines, one can mention 1,2-chalcogenazole N-oxides,^[29] 5-methyltelluro triazoles,^[30] selenocyanates,^[31] Ch-substituted acetylenes^[32-34] or 1,2-dicarba-dodecaborane.^[35] However, to the best of our knowledge, examples of solid-state reactions involving ChB supramolecular assemblies have not been reported so far. We consider here this possibility by exploring the solid-state association and reactivity of a novel diacetylene molecule, whose structural organization within co-crystals is based primarily on strong ChB interactions, without assistance of any HB host matrix.

As a ChB donor, we chose the bis(selenocyanatomethyl)-butadiyne **1** (Scheme 2b). We have shown indeed that organic selenocyanates self-associate in the solid state into regular stacks through short ChB between Se and N \equiv C moieties with Se \cdots N distances down to 2.96 Å, i.e. 0.86 times the sum of van der Waals radii.^[31,36] Taking advantage of this self-recognition process, we hoped that **1** could self-assemble in a similar way, and eventually orient the DA moieties to undergo 1,4-topochemical polymerization. The calculated electrostatic potential (ESP) of the ChB donor **1** confirmed the presence of a strong σ -hole in the prolongation of (N \equiv C)–Se bond with a $V_{s,max}$ value of +52.2 kcal/mol (Fig. S1) and a 2nd, weaker one along the CH₂–Se bond with $V_{s,max}$ value of +33.6 kcal/mol. Compound **1** is prepared from bromination of 2,4-hexadiyne-1,6-diol followed by nucleophilic substitution with KSeCN. All attempts to crystallize **1** were unsuccessful and we therefore envisioned the formation of co-crystals stabilized by ChB interactions, involving ditopic Lewis bases, such as 1,2-bis(4-pyridyl)ethylene (4-bpen) and 1,2-bis(2-pyridyl)-ethylene (2-bpen) as ChB acceptors (Scheme 2b).

In the co-crystal with 4-bpen, **1**•(4-bpen), we observe the formation of chalcogen-bonded 1D chains through very short and linear ChB contacts with a Se \cdots N distance of 2.737 Å, i.e. a RR value of 0.79.

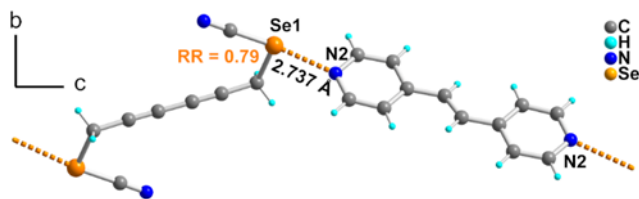


Figure 1. Detail of the ChB interaction (orange dotted lines) in **1**•(4-bpen).^[42]

Molecules **1** are however well separated from each other by the 4-bpen in all directions (Fig. S2) hindering any close contacts between DA moieties and therefore excluding any possibility for polymerization.

With the 2-bpen co-former, a 1:1 co-crystal, **1**•(2-bpen), is also obtained. At variance with previous case, both σ -holes of the Se-atom are engaged in ChB (Figure 2), with (i) the pyridinic nitrogen atom N2 of 2-bpen and (ii) the nitrogen atom N1 of the nitrile group of a neighboring **1** molecule.

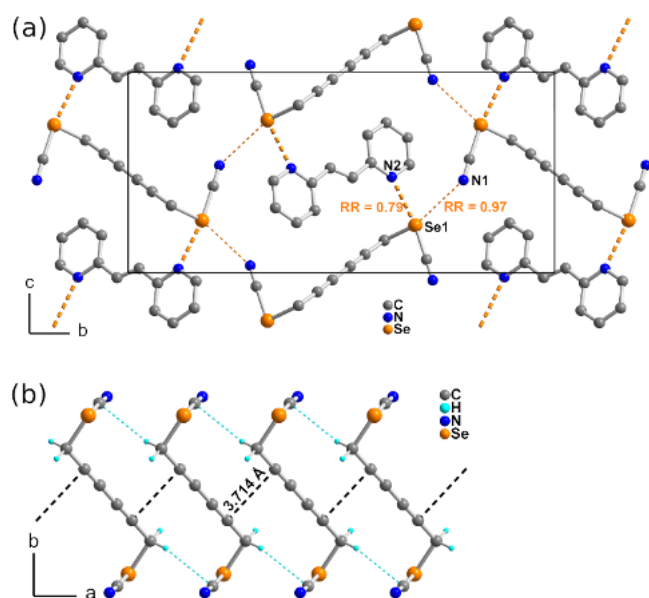


Figure 2. (a) Projection view of the unit cell along *a* axis showing the ChB pattern (orange dotted lines). Hydrogen atoms have been omitted for clarity. (b) Detail of one chain of diacetylene molecules **1** running along *a* axis. Black dotted lines indicate the intermolecular C1...C4' distances required for polymerization, cyan dotted lines indicate the C-H... π (CN) interactions (see text).^[42]

The shortest ChB ($RR = 0.79$) interaction involves the strongest σ -hole in the prolongation of (N \equiv C)–Se bond while a longer one ($RR = 0.97$) involves the weaker σ -hole in the extension of the CH₂–Se bond. Note that both nitrogen atoms have similar ChB acceptor ability, with $V_{s,min}$ values of -38.9 and -40.2 kcal/mol, respectively (Fig. S3). The ranking of different intermolecular interactions in the **1**•(2-bpen) co-crystal is substantiated by calculations^[36] of the total interaction energy E_{tot} for pairs of molecules. As shown in Table S1, the stronger ChB stands first ($E_{tot} = -44.2$ kJ/mol), before π – π stacking between 2-bpen molecules (-30.8 kJ/mol) and between **1** molecules (-29.4 kJ/mol). We also note the setting of C–H... π (CN) interactions (Figure 2b) which develop along the *a* axis between **1** molecules, assembling them with a repeat distance $r = 4.417$ Å, a tilt angle θ (Cf Scheme 1) of 53° , and a C1...C4' distance of 3.714 Å. These structural parameters are compatible with 1,4-topochemical polymerization of DA. Accordingly, we performed irradiation of single crystals of **1**•(2-bpen) with 254 nm UV light, leading only to a slight darkening of the samples. We then considered heating single crystals of **1**•(2-bpen) at 100°C . After 2 h, the color of the crystal changed from light brown to dark brown, while the surface of the crystal starting to deposit some black amorphous powder, with loss of crystallinity. The same experiment was performed on a finely ground powder of **1**•(2-bpen), heated at 100°C under a hot-stage microscope, while small portions were withdrawn at different time intervals to follow the reaction progress by IR spectroscopy, differential scanning calorimetry (DSC) and PXRD.

The time-dependent IR measurements revealed a gradual decrease of an absorption peak at 2145 cm^{-1} , accompanied by the appearance of a new peak at 2051 cm^{-1} (Fig. 3). DFT calculations on the starting diacetylene **1** reveal that the peak at 2145 cm^{-1} corresponds to a combined stretching frequency of $\text{C}\equiv\text{C}$ and $\text{C}\equiv\text{N}$ moieties (Fig. S4). On the other hand, the new band at 2051 cm^{-1} has been already attributed to a $\text{C}\equiv\text{C}$ stretching frequency in several poly(diiododiacetylene) structures, also accompanied with a shift toward lower frequencies upon polymer formation.^[20]

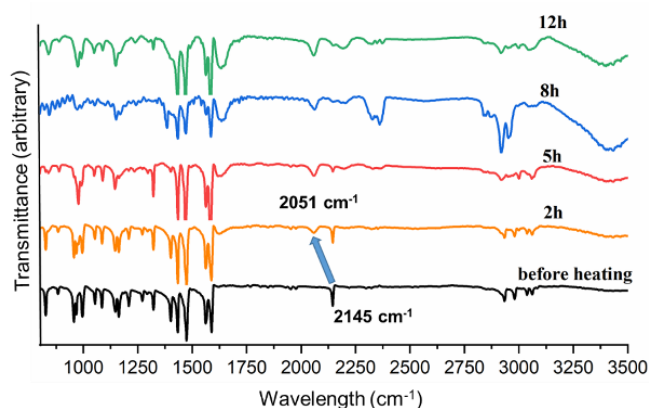


Figure 3. Time-dependent reaction progress in co-crystal **1•(2-bpen)** by IR spectroscopy.

Thus, this new peak is unambiguously attributed to the PDA backbone. After 8 h, the original absorption at 2145 cm^{-1} had almost vanished, an indication of completion of the reaction. The small peak remaining at 2145 cm^{-1} even after polymerization probably corresponds to CN stretching frequency of the polymer. In a control experiment, we also followed by IR spectroscopy the heating at 100°C of a powdered sample of **1** alone. We didn't observe any change in the IR spectrum even after heating for 15 h and the sample remained crystalline in nature (Fig. S5).

Also, to our surprise, while the powder of **1•(2-bpen)** was heated under the hot-stage microscope, some white crystals start to deposit on the surface of the polymerized sample (Figure 4). These white crystals were harvested during the course of heating and ^1H -NMR showed them to be the pure ChB acceptor 2-bpen.

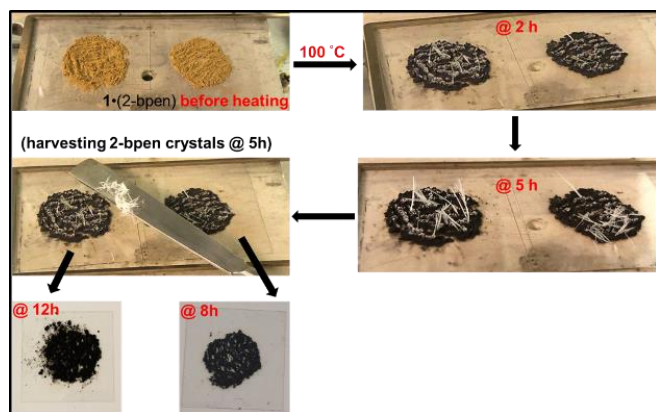


Figure 4. Evolution of **1•(2-bpen)** upon heating, highlighting recrystallization of the sublimed 2-bpen.

This phenomenon is most probably a consequence of the mismatch between the co-crystal periodicity ($r = 4.417\text{ \AA}$) and the expected 4.9 \AA periodicity of polydiacetylene (see Scheme 1).^[37,38] In this context, 2-bpen molecules are left unbounded in the polymeric network and sublime under the experimental conditions (cf. mp of 2-bpen = 120°C) to recrystallize between the plates of the hot-stage microscope. The 2-bpen molecules can sublime from the molecular channels formed along the a axis (Fig. 2a) which is also the polymerization axis. Further heating for 8 to 12 h completely removed the 2-bpen molecules from the polymerized sample, producing a fine black powder. This phenomenon not only allows us to obtain a pure PDA polymer but also to recover 2-bpen in an essentially

quantitative manner. It comes in stark contrast with the usual DA polymerization based on strong hydrogen-bonded host matrices which stay embedded in the final polymer.

These results were further substantiated by DSC measurements, as shown in Fig. 5a for respectively, **1**, 2-bpen and **1**•(2-bpen). The co-crystal **1**•(2-bpen) shows an exothermic peak around 100°C associated with the topochemical reaction and a small peak around 120°C that coincides with the mp of 2-bpen, following its sublimation (see above). On the other hand, **1** alone shows a completely different behavior, with a small endothermic peak slightly above 120°C which then merges with an exothermic peak, indicating that **1** is first melting around 120°C to then undergo random polymerization in the molten state. It also demonstrates that **1** alone doesn't show any reactivity when heated at 100°C, as already observed by IR spectroscopy. Fig. 5b represents the DSC profile of reaction progress. After heating the co-crystal **1**•(2-bpen) for 2 h, we observe a reduction in the exothermic peak associated with the partial polymerization. After 5.5 h, the disappearance of this exothermic peak is an indication of completion of the reaction, leaving only the melting peak of the sublimed 2-bpen. Co-crystal heated for 8 or 12 h don't show any peak, suggesting completion of the reaction as well as sublimation of 2-bpen.

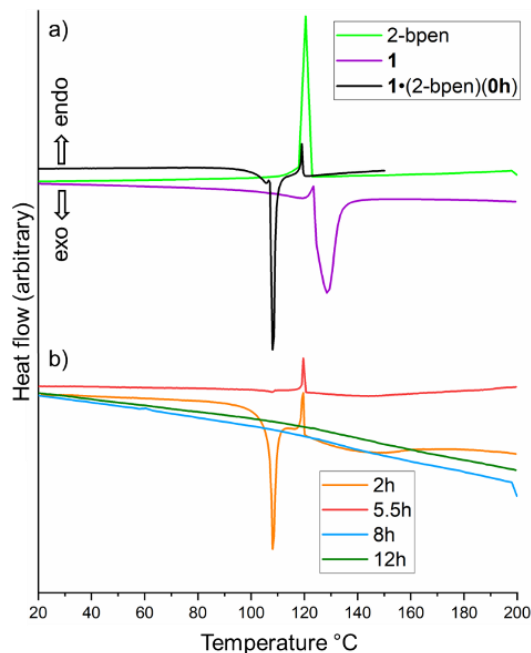


Figure 5. a) DSC traces (heating rate 1°C/min) for 2-bpen and **1**, and for co-crystal **1**•(2-bpen) before polymerization. (b) DSC traces of samples of **1**•(2-bpen) taken during polymerization (at 100°C) at specified times.

Temperature-dependent PXRD experiments were performed in a sealed capillary and data were collected at different time intervals. The RT PXRD pattern of **1**•(2-bpen) matches very well with the pattern simulated from its single-crystal X-ray structure, demonstrating the purity of the sample (Fig. 6). The heating profile shows that as soon as temperature reaches 100°C the original set of diffraction peaks starts to fade and a new set of peaks appears on the spectrum (Fig. S6). The PXRD spectrum after 12 h shows a broad hump in the low angle region, characteristic of an amorphous phase with a new set of peaks which happen to match with the simulated PXRD pattern of a known crystal phase of 2-bpen.^[39] These results demonstrate the amorphous nature of obtained PDA polymer and also confirm the sublimation and recrystallization of 2-bpen during the polymerization. Furthermore, gas physisorption experiments showed that the solid is essentially non-porous (or macro-porous) with a specific surface area of 9 m²/g (Fig. S7).

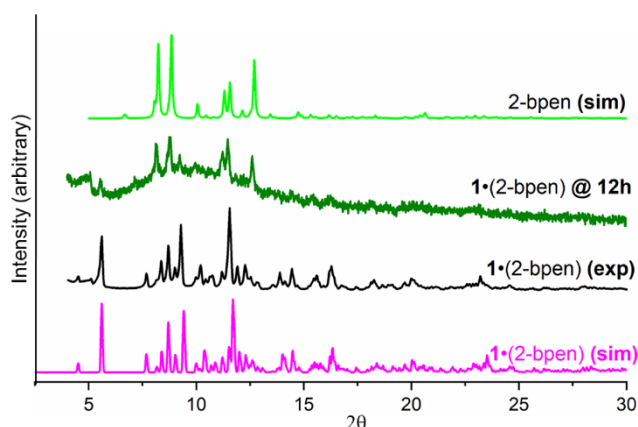


Figure 6. Comparison of PXRD spectra of pristine and heated sample with their stimulated pattern.

PDA polymers are known to show a significant enhancement in their conductivity upon iodine doping by hole creation in the PDA backbone.^[9,40] The RT conductivity of the undoped sample (Fig. 7a), $\sigma_{300K} = 7.2 \times 10^{-13}$ S/cm, falls in the 10^{-10} – 10^{-14} S/cm range for undoped PDA polymers.^[41] The doping was performed by placing the sample in an iodine chamber at 35°C for 6 days. Allowing the sample to rest in air for 3 days gave a stable room-temperature conductivity of $\sigma_{300K} = 2.6 \times 10^{-5}$ S/cm (Fig. 7b, blue), i.e. a 8 orders of magnitude enhancement relative to the undoped sample, only slightly decreased to $\sigma_{300K} = 7.9 \times 10^{-6}$ S/cm after several washings with CH_2Cl_2 (Fig. 7b, green). EDS analysis gives a $\approx 2:1$ Se:I molar ratio (64:36), i.e. one triiodide I_3^- per $(\text{C}_8\text{H}_4\text{N}_2\text{Se}_2)_3$ unit.

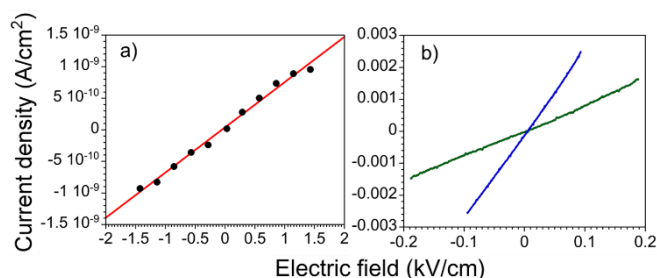


Figure 7. I-V plots for a) undoped sample b) doped sample after exposing to air for 3 days (blue) and subsequent DCM washing (green).

In conclusion, we have reported here the first example of a solid-state reaction within a ChB assembly. Specifically, ChB interactions between a novel organic selenocyanate-substituted diacetylene (**1**) and a ditopic Lewis base (2-bpen) successfully organized diacetylene moieties into a reactive orientation for 1,4-polymerization. Thermally-induced topochemical polymerization of **1**•(2-bpen) and the formation of PDA backbone were confirmed by time-dependent IR and DSC measurements. Remarkably, polymerization in this ChB co-crystal was accompanied by sublimation of the ChB acceptor molecules (2-bpen), providing the PDA polymer in a pure form with quantitative recovery of 2-bpen. This behavior is in contrast to the commonly used HB co-crystal strategy relying on strong hydrogen-bonded host matrix, which then stay always embedded in the final PDA polymer. An increase in conductivity by 8 orders of magnitude upon iodine doping further proved the formation of PDA polymer. In a more prospective way, the ability of the selenocyanate group to act as a good leaving group toward nucleophilic substitution could also allow now for post-functionalization of the polymer to tune its properties. Altogether, these results demonstrate the high potential of chalcogen bonding as a very efficient tool to achieve supramolecular control toward solid-state reactivity.

Acknowledgements

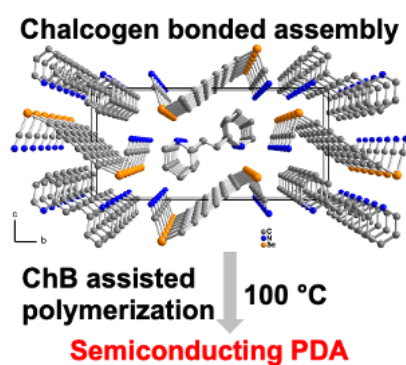
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- [42] CCDC 2116274 [1•(4-bpen)] and 2116273 [1•(2-bpen)] contain the supplementary crystallographic data for this paper. These data are provided free of charge by the Cambridge Crystallographic Data Centre.

Entry for the Table of Contents



No strong hydrogen bonding but weaker chalcogen bonding (ChB) interactions are used for the first time to organize diacetylene molecules in the solid state for thermal topochemical polymerization. The obtained polydiacetylene, free of the pyridine-based ChB acceptor, exhibits 8 orders of magnitude increase in conductivity upon iodine doping.