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Synthesis and Transfer of Chirality in Supramolecular Hydrogen Bonded Conjugated Diblock Copolymers

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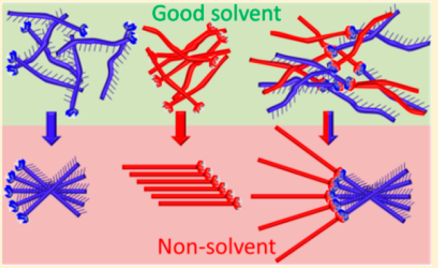
Supporting Information

ABSTRACT: The synthesis of a block copoly(3-alkylthiophene) consisting of two different P3AT blocks equipped with an H-donor and -acceptor functionality is presented. The P3ATs were synthesized using a functionalized Ni-initiator. By a series of postpolymerization reactions, including click chemistry, an H-donor and -acceptor entity was attached to the end of the polymer chains. Evidence for a quantitative functionalization of the polymers was provided by ^{1}H NMR and MALDI-ToF analyses. Chiral side chains were implemented on one of both blocks, allowing the study of the influence of the H-bond formation on the chiral self-assembly using UV−vis and circular dichroism spectroscopy.



INTRODUCTION

Different methodologies have been developed in the past to obtain advanced macromolecular structures. Most of those procedures rely on the creation of covalently bonded macromolecules. Nevertheless, in the past decades, noncovalent interactions, with a special emphasis on hydrogen bonds, have triggered more and more interest from different research groups and can now be regarded as an extra toolbox.[1]

Multiple hydrogen bonds (MHBs) have shown to be versatile, and by making use of the directional character of the interaction, different kinds of highly structured entities can nowadays be obtained. One way of exploiting H-bonding in polymer science is the formation of so-called pseudo block copolymers, i.e. supramolecular block copolymers designed using various building blocks, such as poly(benzyl methacrylate) and poly(*n*-butyl acrylate),[2] self-complementary poly(alkyl acrylates),[3] and telechelic poly(isobutylene)s and poly(ether ketone)s.[4] The H-bonding is not only limited to two blocks but also led to the development of polymers of a supramolecular nature.[5−7] These interactions were also implemented in conjugated entities such as perylenes.[8] Meijer et al. extended the work on conjugated assembly by focusing on chiral oligo(*p*-phenylenevinylene)perylene bisimide.[9] This led to the further development of conjugated polymer networks for applications such as organic photovoltaics.[10,11]

Contrarily to their nonconjugated counterparts, conjugated polymers (CP) equipped with H-bonding entities have not yet been so extensively employed. The ability to obtain poly(3-alkylthiophene)s (P3AT)s[12−15] and some other conjugated polymers[16−29] via a controlled chain-growth polymerization has opened new platforms to synthesize CPs with low dispersities, predictable molar masses, and perfect control over the molecular structure. Hence, it also provides the possibility to prepare all-conjugated block copolymers by successive monomer addition[24,30−50] and even control over the end-groups. In the specific case when Ni(dppp) is used as a catalyst, H/Br-terminated CPs are obtained.[14,15] As far as the end-functionalizing of the conjugated polymers is concerned, different approaches can be used. In the case of a controlled chain-growth polymerization, a Grignard reagent equipped with a functional group can be added at the end of the polymerization.[51−54] The main drawback of this approach is that it requires a controlled polymerization, which is only the case for a selected number of CPs. The approach also suffers from the fact that both mono- and dicapping can occur,[51−54] leading to a sample that is contaminated with polymers containing two functional groups. A second approach makes use of postpolymerization reactions: the Br atom can be converted into carboxylic acid by making use of a GRIM reaction and the addition of CO_2,[55] or an aldehyde function can be introduced at the H-terminated thiophene by a Vilsmeier reaction.[56] A third method makes use of an initiator which is equipped with a functional group. This requires the polymerization to proceed via a chain-growth mechanism, but the polymerization does no longer need to be controlled. Applied to P3ATs, this concept results in polymers end-capped at one end with the functional group of the initiator and at the other end with a H atom. Different functionalized polymers have

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already been obtained by this method.[57−62] The functional groups make it possible to form a diblock conjugated copolymer that cannot be synthesized by successive monomer addition.[58,60,63] Another asset is that they can be used to decorate nanoparticles (NPs).[53] We recently prepared a variety of such hybrid materials using different functional groups and nanoparticles.[64]

Hardeman et al. showed that these functionalized initiators are not restricted to form covalent bonds but can also be used as partners for noncovalent interactions such as single H-bonds in the formation of graft copolymers.[65] Besides these single hydrogen bond P3ATs, Enders et al. reported oligo- and polythiophenes with MHB moieties.[66] In the present work, we report the formation of a block copolymer (Figure 1)

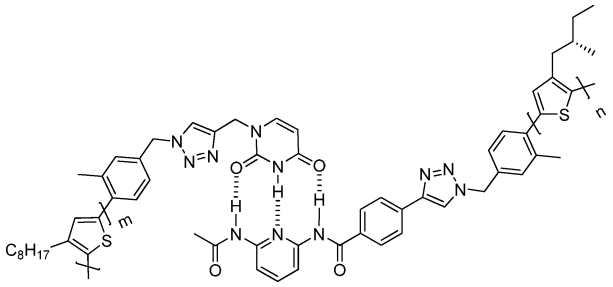

Figure 1. Block copolymer formed by MHB.

composed of two conjugated P3AT blocks, by noncovalent interactions, more in particular MHBs. MHBs rather than single H-bonds will be used to increase the interaction strength. By introducing chiral alkyl side chains on one block, the stacking behavior of the different blocks can be monitored, and the influence of the block copolymer formation on the self-assembly can be studied. Previous studies have indicated that the block that aggregates first imposes an influence on the stacking behavior of the other block.[46,63] Here it will be tested whether this principle also holds when the block copolymer formation is realized by supramolecular H-bond formation (Figure 1).

EXPERIMENTAL SECTION

All reagents were purchased from TCI, Sigma-Aldrich, Acros Organics, and ABCR. Reagent grade solvents were dried by a solvent purification system MBRAUN SPS 800 (columns with activated alumina). The precursor initiator **1**,[63] 2-acetamido-6-aminopyridine (**5**),[67] 4-ethynylbenzoyl chloride (**6**),[68] and the precursor monomers **3a**[46] and **3b**[46] were synthesized according to literature procedures.

The gel permeation chromatography (GPC) measurements were performed using a Shimadzu 10A apparatus with a tunable absorbance detector and a differential refractometer in THF as eluent calibrated toward polystyrene standards. ^{1}H and ^{13}C nuclear magnetic resonance (^{1}H NMR) measurements were carried out with a Bruker Avance 300, 400, and 600 MHz. Mass spectra were recorded using an Agilent HP5989. Matrix-assisted laser desorption ionization-time-of-flight (MALDI-ToF) mass spectra were recorded using a Waters QToF Premier mass spectrometer equipped with a nitrogen laser of 337 nm with a maximum output of 500 J/m^2 delivered to the sample in 4 ns pulses at 20 Hz repeating rate. Time-of-flight mass analyses were performed in the reflection mode at a resolution of about 10 000. The matrix, *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]-malonitrile (DCTB), was prepared as a 40 mg/mL solution in chloroform.[69] The matrix solution (1 μL) was applied to a stainless steel target and air-dried. Polymer samples were dissolved in chloroform to obtain 1 mg/mL solutions. Then, 1 μL aliquots of these solutions were applied onto the target area (already bearing the matric crystals) and then air-dried. FT-IR spectra were recorded using a Bruker Alpha-p apparatus in ATR mode. UV−vis and circular dichroism (CD) measurements were performed on a PerkinElmer Lambda 900 UV−vis NIR and a JASCO 62 DS apparatus, respectively.

Synthesis of *N*-(6-Acetamidopyridin-2-yl)-4-ethynylbenzamide (7). **5** (500 μmol, 75.6 mg), 4-(dimethylamino)pyridine (DMAP) (10.0 μmol, 1.22 mmol), and triethylamine (TEA) (550 μmol, 76.2 μL) were dissolved in dry THF (2.5 mL) under a N_2 atmosphere. This mixture was added dropwise to a solution of **6** (0.50 mmol, 82.3 mg) in dry THF (1 mL). The reaction mixture was refluxed for 30 h and cooled to room temperature. Subsequently, the mixture was extracted with ethyl acetate and washed with brine. The organic layers were collected and dried over $MgSO_4$, and the solvents were removed under reduced pressure. The product was purified using column chromatography on silica gel, eluting with ethyl acetate. The product was isolated as a white solid. Yield: 19.6 mg (14%). ^{1}H NMR ($CDCl_3$): δ = 8.23 (s, 1H), 8.06 (d, J = 8.2 Hz, 1H), 7.94 (d, J = 8.2 Hz, 1H), 7.86 (d, J = 8.6 Hz, 2H), 7.77 (t, J = 8.2 Hz, 1H), 7.63 (d, J = 8.6 Hz, 2H), 7.60 (s, 1H), 3.25 (s, 1H), 2.22 (s, 3H). ^{13}C NMR ($CDCl_3$): δ = 168.48, 164.61, 149.52, 149.36, 141.10, 132.58, 127.11, 126.30, 109.84, 109.71, 82.51, 80.21, 24.81. MS: m/z = 279 (M^+), 237 ($M^+ - CH_3CO$). Melting point: 191.3−193.6 °C.

Synthesis of 1-(Prop-2-ynyl)pyrimidine-2,4-dione (8). Hexamethyldisilazane (HMDS) (15.5 mmol, 2.50 g) and trimethylsilyl chloride (TMSCl) (1.60 mmol, 174 mg) were dissolved in dry acetronitrile (20 mL) under an argon atmosphere, and the mixture was added dropwise to a solution of uracil (4.00 mmol, 448 mg) in dry acetonitrile under an argon atmosphere. The mixture was refluxed for 4 h and was then cooled to room temperature, after which propargyl bromide in toluene (4.80 mmol, 80 wt %, 714 mg) and KI (10.0 μmol, 1.67 mg) were added to the solution. The mixture was then refluxed for 16 h, extracted with ethyl acetate, and washed with $NaHCO_3$ and brine. The product was dried over $MgSO_4$, and the solvents were removed under reduced pressure. The product was purified using column chromatography on silica gel, eluting with ethyl acetate/methanol (97/3). The product was obtained as white crystals. Yield: 186 mg (31%). ^{1}H NMR ($CDCl_3$): δ (ppm) = 8.66 (s, 1H), 7.46 (d, J = 8.2 Hz, 1H), 5,79 (dd, J = 8.2 Hz, J = 1.6 Hz, 1H), 4.56 (d, J = 2.6 Hz, 2H), 2.50 (t, J = 2.5 Hz, 1H). Melting point: 167.8−170.4 °C.

Synthesis of P1a. The precursor initiator **1** (50.0 μmol, 44.9 mg) and 1,3-bis(diphenylphosphino)propane (dppp) (100 μmol, 41.2 mg) were dissolved in dry THF (4 mL), purged with argon, and stirred for 15 min. Subsequently, monomer **4a** in dry THF (8.67 mL) was purged with argon and added to the initiator solution. For the synthesis of **4a**, the precursor monomer **3a** (1.00 mmol, 359 mg) was dissolved in dry THF (8 mL) and purged with argon, and *i*-PrMgCl·LiCl (1.28 M in THF, 1.00 mmol, 0.87 mL) was added to the solution. The reaction was stirred for 60 min at room temperature. To verify the conversion, a small aliquot (0.2 mL) was quenched with D_2O after 30 min and analyzed by ^{1}H NMR. After polymerizing for 1 h, the reaction mixture was terminated with a 2 M HCl solution. The mixture was concentrated, and the polymer was precipitated in MeOH. Next, the polymer was filtered and fractionated by Soxhlet extraction with methanol and chloroform. The chloroform fraction was concentrated, and the polymer was precipitated in methanol, filtered, and dried in vacuo. The final polymer was recovered as a dark red-brown solid. Yield: 90.0 mg (59%).

Synthesis of P1b. The same procedure as described for **P1a** was followed, using **3b** (1.00 mmol, 401 mg). Yield: 128 mg (62%).

Synthesis of P2a. **P1a** (283 μmol, 43.1 mg) was dissolved in THF (50 mL), purged with argon, and shielded from light. Tetrabutylammonium fluoride trihydrate (TBAF·3H_2O) (340 μmol, 107 mg) was added, and the reaction was stirred at room temperature for 16 h. Water was added and extracted with $CHCl_3$, dried over $MgSO_4$, and concentrated. The polymer was precipitated in methanol, filtered, and dried in vacuo. **P2a** was obtained as a dark red-brown solid. Yield: 39.0 mg (90%).

Synthesis of P2b. The same procedure as described for **P2a** was followed, using **P1b** (518 μmol, 101 mg) and TBAF·3H_2O (622 μmol, 196 mg). Yield: 93.0 mg (92%).

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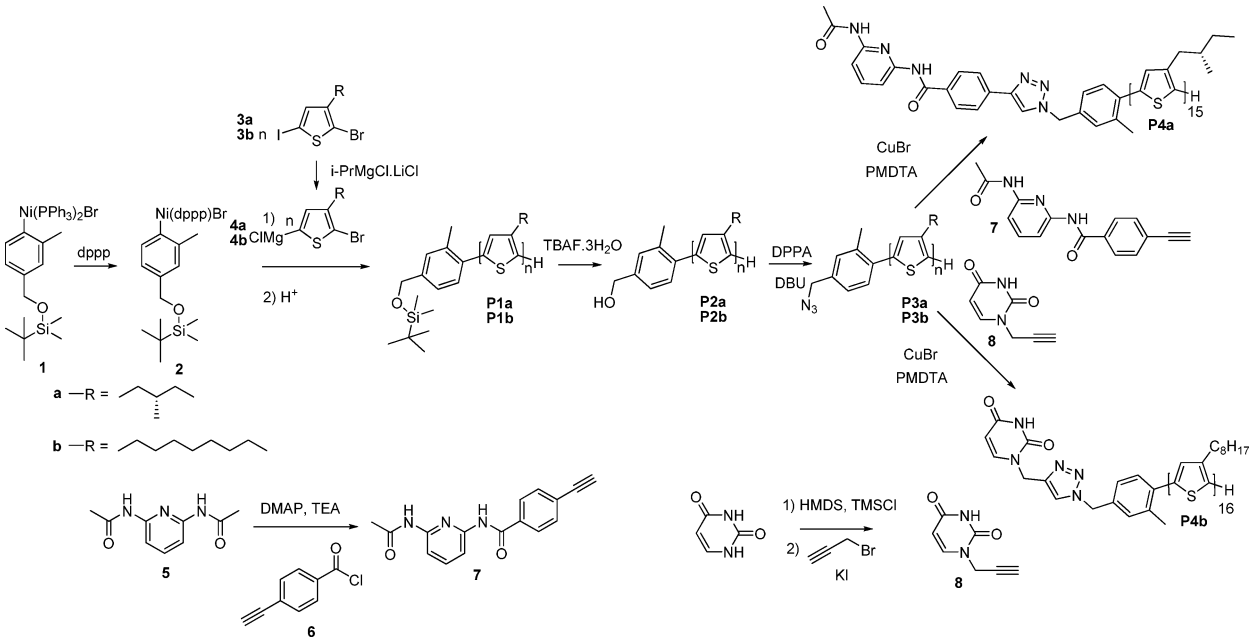
Scheme 1. Overview of the Polymer Synthesis Including Polymerization of 4a and 4b with the Use of Initiator 2, Followed by the Different Postpolymerization Reactions Yielding P4a and P4b, and Synthesis of the Hydrogen Donor 7 and Acceptor 8 Entities



Synthesis of P3a. **P2a** (158 μmol, 24.0 mg) was dissolved together with diphenylphosphoryl azide (DPPA) (3.15 mmol, 867 mg) in dry THF (60 mL) and cooled to 0 °C, and then 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (3.15 mmol, 480 mg) was added. The mixture was stirred for 12 h at room temperature, concentrated, and precipitated in methanol. Subsequently, the polymer was washed thoroughly with methanol and dried under vacuo. **P3a** was recovered as a dark red-brown solid. Yield: 21.3 mg (89%).

Synthesis of P3b. The same procedure as described for **P3a**. **P2b** (400 μmol, 79 mg), DPPA (8.00 mmol, 2.20 g), and DBU (8.00 mmol, 1.22 g) were used. Yield: 67.0 mg (86%).

Synthesis of P4a. An argon-purged solution of *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDTA) (9.03 μmol, 1.56 mg) in dry THF (20 mL) was added to a suspension of CuBr (6.78 μmol, 970 μg) in dry THF (20 mL). To this mixture, a solution of **P3a** (113 μmol, 17.2 mg) and **7** (612 μmol, 170 mg) in dry THF (200 mL) was added. The mixture was stirred for 24 h under an argon atmosphere. Then, an aqueous solution of NH_3 was added. The mixture was subsequently extracted with $CHCl_3$, dried over Na_2SO_4, concentrated, precipitated in methanol, and filtered. **P4a** was obtained as a dark red-brown solid. Yield: 13.4 mg (79%).

Synthesis of P4b. The same procedure as described for **P4a** was followed, using **P3b** (214 μmol, 45 mg), **8** (1.16 mmol, 174 mg) PMDTA (18.5 μmol, 3.21 mg), and CuBr (13.9 μmol, 1.99 mg). Yield: 43.0 mg (96%).

RESULTS AND DISCUSSION

Polymer Synthesis. For the synthesis of P3ATs equipped with H-donor and -acceptor entities, it is important to realize that Grignard monomers (**4a** and **4b**, Scheme 1) are employed during the polymerization. Since Grignard reagents are incompatible with acidic entities (H-donors), different postpolymerization reactions, including click chemistry procedures, are employed to introduce the functionality. Therefore, a protected alcohol Ni-initiator[63] is synthesized and used in the polymerization.

The functional Ni-initiator was prepared by a oxidative insertion of $Ni(PPh_3)_4$ in an appropriately functionalized *o*-tolyl bromide. The *o*-tolyl group was used to enhance the stability against disproportionation.[57] Since the polymerization requires the use of Grignard monomers, protection of the alcohol function is needed.

Polymers **P1a** and **P1b** were synthesized with the Ni(dppp)-mediated polymerization. Therefore, the precursor monomers 2-bromo-5-iodo-3-alkylthiophene (**3a** and **3b**) were converted to the actual monomers 5-magnesiochloro-2-bromo-3-alkylthiophene (**4a** and **4b**) using *i*-PrMgCl·LiCl. Prior to the initiation, a ligand exchange using 2 equiv of dppp was performed (Scheme 1). The dppp ligand, in contrast to PPh_3 present in **1**, results in a controlled polymerization.[57] Hereby, we were able to tune the polymerization degree (DP) by varying $[M]_0/[In]$. This ratio was set to 20 for both polymerizations. The polymerization was terminated after 1 h by treating the mixture with a 2 M HCl solution in THF.

Molar masses and dispersities of **P1a** and **P1b** (Table 1) were determined by GPC toward polystyrene standards. It is important to note that GPC tends to overestimate the molar mass of P3ATs.[70] For both polymers low dispersities were obtained, which is in line with the controlled nature of the polymerization.

Table 1. $\bar{M}_n$, $Đ$, and DP for P1a and P1b

polymer	$\bar{M}_n{}^a$ (kg/mol)	$Đ^a$	DP^b
P1a	3.6	1.1	15
P1b	5.3	1.1	16

[a]Determined by GPC in THF toward polystyrene standard. [b]Determined by ^{1}H NMR

A part of the ^{1}H NMR spectra of **P1a** and **P1b** is presented in Figure 2. The spectrum of **P1a** shows the *o*-tolyl function of the initiator at 2.49 ppm (a), the doublet of multiplets at 2.70 ppm originating from the internal α-methylene protons (b), and more upfield a part of a multiplet of a doublet originating from the terminal α-methylene (c). Note that in the figure only the upfield part of the doublet of c is integrated due to

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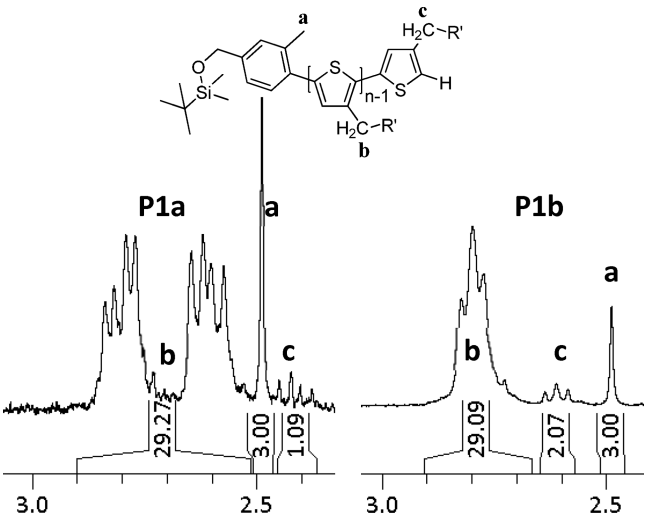

Figure 2. Zoom of the α-methylene and *o*-tolyl region of **P1a** (left) and **P1b** (right).

overlapping signals. A DP of 15 (Table 1) was derived from the integration values using eq 1 with $x = 1$ (only half of the signal is integrated).

$$\mathrm{DP} = \frac{b + c}{\frac{a}{3} + \frac{c}{x}} \quad (1)$$

The same pattern is also observed in the spectrum of **P1b**: the *o*-tolyl function of the initiator at 2.49 ppm (a), a broad triplet at 2.80 ppm originating from the internal α-methylene protons (b), and more upfield a triplet originating from the terminal α-methylene (c) which corresponds to a H-terminated unit. Here, it is clear that the α-methylene protons of Br-terminated thiophene, resonating at 2.57 ppm,[46,71] are not observed in the ^{1}H NMR spectrum. This indicates that the polymerization proceeded in a controlled manner. A DP of 16 (Table 1) was calculated using the integration values ($x = 2$) from Figure 2 in combination with eq 1.

MALDI-ToF analysis (Figure 3) of **P1a** and **P1b** shows that all chains were indeed initiated by the external initiator and that the chains were H-terminated, indicating the high degree of control over the polymerization, which is in line with the ^{1}H NMR analysis.

Postpolymerization Reactions. After preparation of the protected P3ATs, a series of postpolymerization reactions were performed on **P1a** and **P1b** (Scheme 1) in order to obtain the hydrogen donor and acceptor functionalized P3ATs. It is important to note that all postpolymerization reactions must be quantitative. Their conversion was monitored by ^{1}H NMR spectroscopy (Figure 4). In particular, the signal corresponding to the CH_2 next to the functional group was monitored. In a first step, the silyl protecting group was removed by the use of TBAF·3H_2O. Upon deprotection, a small shift in the ^{1}H NMR from 4.74 (**P1a** and **P1b**) to 4.71 ppm (**P2a** and **P2b**) can be observed. Next, the alcohol function was converted to an azide with DBU and DPPA, resulting in a shift from 4.71 (**P2a** and **P2b**) to 4.34 ppm (**P3a** and **P3b**).

Finally, in a last postpolymerization step, the donor (**7**) and acceptor (**8**) units were coupled to the azide groups using a Cu(I)AAC click reaction. ^{1}H NMR indicated a shift to 5.60 ppm for the CH_2 in **P4a** and 5.49 ppm for **P4b** was observed. Note also the presence of the singlet at 4.9 ppm, originating from the H-acceptor moiety, where it shifts from 4.6 ppm before the coupling to 4.9 ppm after the coupling. Besides ^{1}H NMR spectroscopy, FT-IR measurements also supported the quantitative conversion (Figure S20).

For the synthesis of **7** (Scheme 1), acetyl chloride was reacted with 2,6-diaminopyridine to yield **5**. After purification, 4-ethynylbenzoyl chloride (**6**)[68] was added in order to produce the donor unit **7**. The acceptor unit **8** (Scheme 1) was synthesized starting from uracyl, following a two-step procedure that involves the addition of hexamethyldisilizane and trimethylsilyl chloride, followed by the addition of propargyl bromide and KI.

MALDI-ToF analysis of **P4a** and **P4b** (Figure 5) shows that after a series of three postpolymerization reactions the polymer chains were still all H-terminated and equipped with the correct acceptor or donor entity. MALDI-ToF spectra of all polymers are presented in the Supporting Information (Figures S4–S11).

^{1}H NMR Analysis as Evidence for MHB Formation. For the study of the self-assembly of the supramolecular block copolymer, solvents are required to allow the formation of the

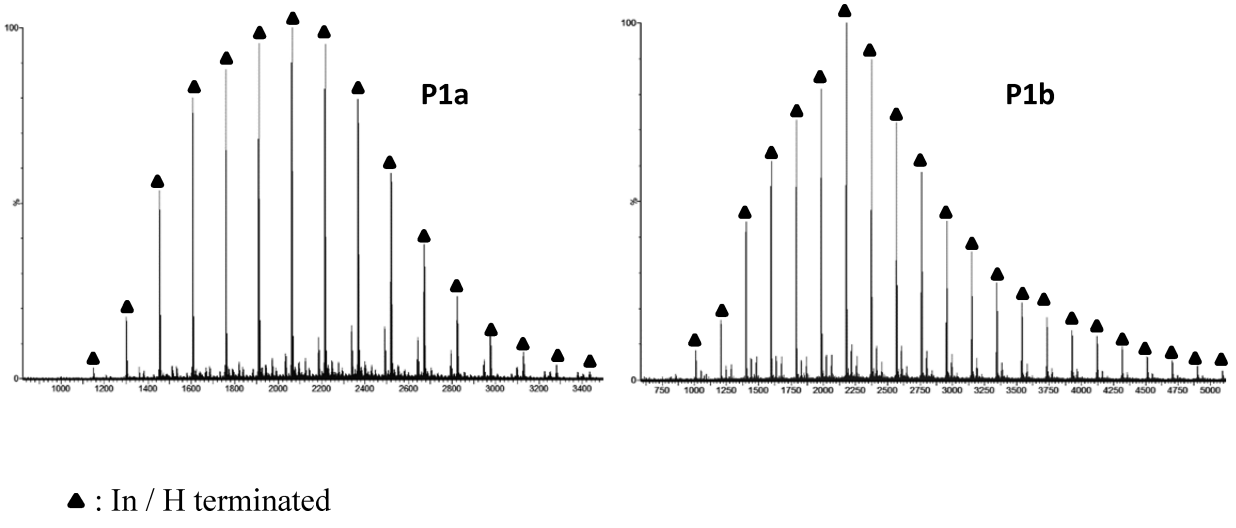

Figure 3. MALDI-ToF spectra of **P1a** (left) and **P1b** (right).

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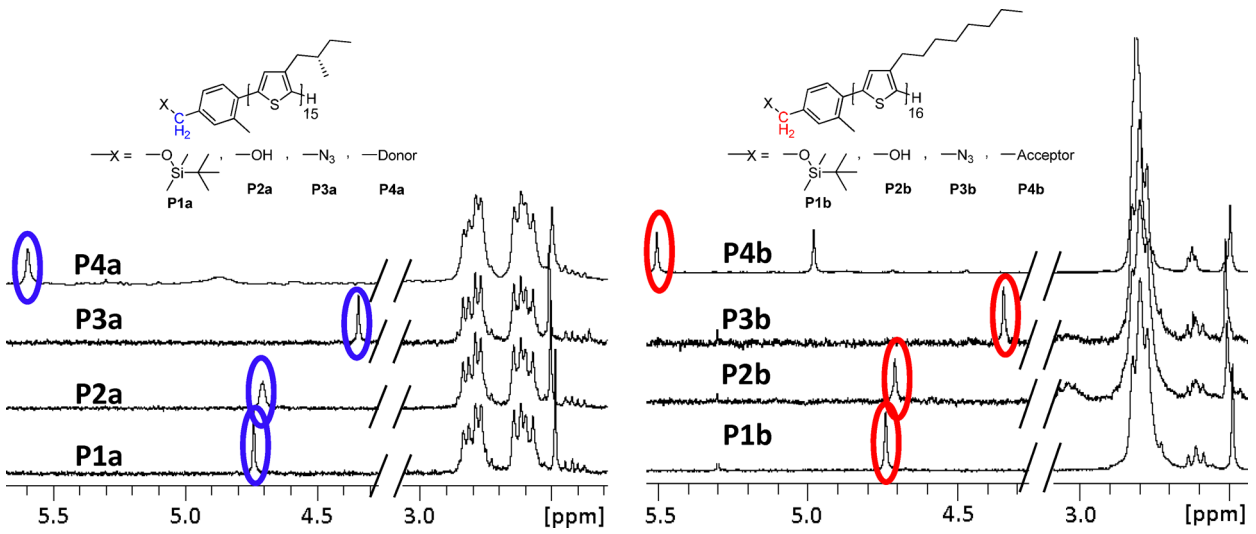

Figure 4. ^{1}H NMR spectrum of postpolymerization of **P1a**−**P4a** (left) and **P1b**−**P4b** (right).

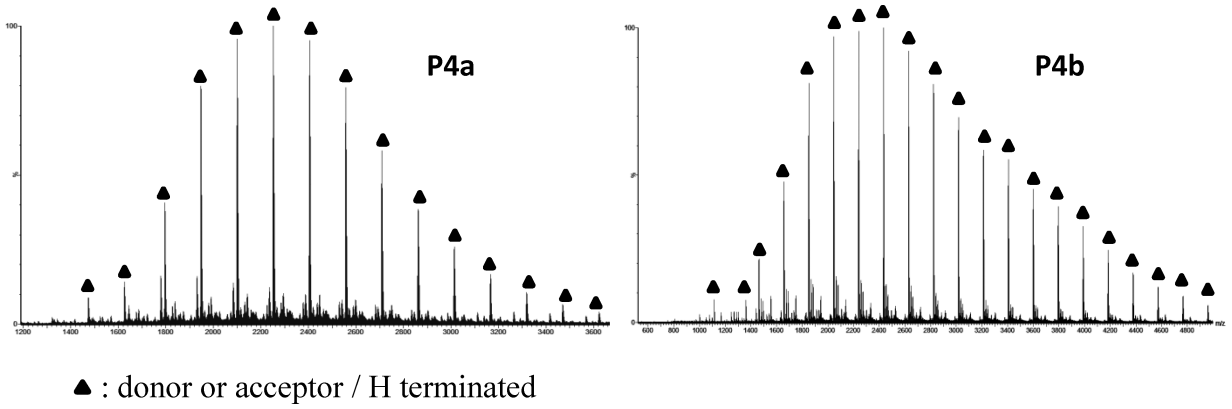

Figure 5. MALDI-ToF spectra of **P4a** (left) and **P4b** (right).

H-bonds. The ^{1}H NMR spectra of the donor (**7**), the acceptor (**8**), and an equimolar mixture of **7** and **8** in different solvents and solvent mixtures are presented in Figure 6. Upon H-bond formation, the NMR spectra of **7**, **8**, and the **7** + **8** mixture are expected to be different, highlighting then the formation of the noncovalent complexes. For the self-assembly studies, two different solvents are required. The first solvent must dissolve both **P4a** and **P4b**, while remaining compatible with the subsequent formation of H-bonds. In a second step, we will add a nonsolvent that result in the self-assembly but leaves the H-bonds intact.

THF and $CHCl_3$ are able to solubilize poly(3-alkylthiophene)s and are candidates as good solvent. Acetonitrile is able to precipitate the polymers and might also keep the H-bonded entities interacting with each other. Note that methanol, being a protic solvent, was obviously not considered. For all experiments described below, 0.5 mM deuterated solutions of **7**, **8**, and mixture of **7** and **8** were prepared. When THF-d_8 was used as a solvent, no difference (Figure S21) between the ^{1}H NMR spectra for the donor or acceptor and the mixture of both was observed, demonstrating that the H-bonds are disrupted in THF. Therefore, THF is not the appropriate solvent for these aggregation studies. $CDCl_3$, in contrast, did induce significant differences between the ^{1}H NMR data for the mixture and the individual compounds. Indeed, a clear shift is observed for the amide protons (a, e, and a′) as well as for the other protons (b, c, d, f, g, and b′), concluding that $CHCl_3$ can be used as solvent for these aggregation experiments (Figure 6). By using a solvent mixture of $CDCl_3$/CD_3CN (50/50), obvious shifts were observed as well. This provides the evidence that upon addition of CH_3CN the polymer not only self-assembles but also that the H-bonds are not disrupted.

Next, it is investigated whether the H-bonds are also formed between the functionalized polymers. Since the polymers start to precipitate in CD_3CN, the ^{1}H NMR spectrum is only recorded in $CDCl_3$. Again, ^{1}H NMR was recorded for **P1a**, **P1b**, and an equimolar mixture of both polymers (Figure 7), based on the DP values determined from the ^{1}H NMR spectra. It is clear that the amide protons a and a′ are strongly shifted in the mixture spectrum, indicating that H-bonds are indeed formed. Also, small shifts can be observed for several other protons such as b, c, d, b′, and c′.

Self-Assembly Study. Polymers **P4a** and **P4b** and an equimolar mixture of **P4a** and **P4b** were subjected to a solvatochromism experiment. By using a mixture of the H-donor and -acceptor polymers and comparing the results which the spectra obtained from the separate polymers (**P4a** and **P4b**), the effect of H-bond formation, i.e. block copolymer, on the stacking behavior can be monitored by CD spectroscopy. In the solvatochromism experiment, CH_3CN is gradually added as a nonsolvent to $CHCl_3$ solutions of **P4a**, **P4b**, and a 1:1 mixture

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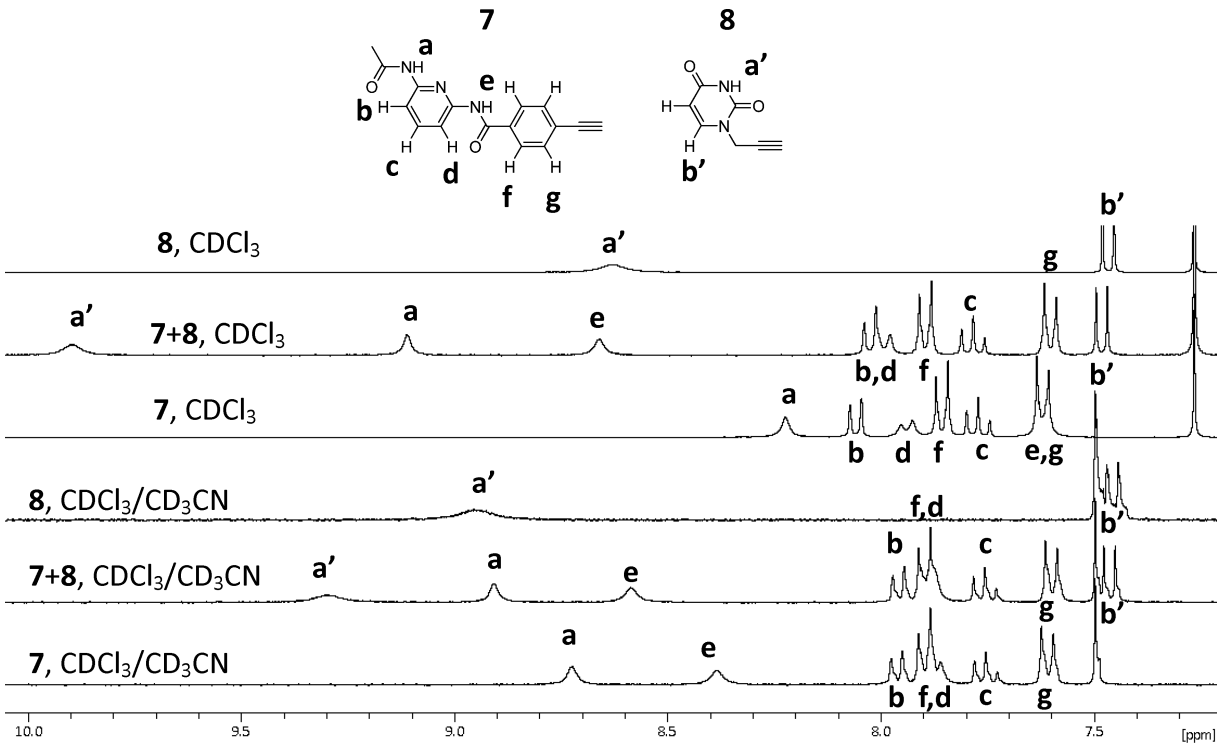

Figure 6. ^{1}H NMR of 7, 8, and 7 + 8 in $CDCl_3$ (top three spectra) and in $CDCl_3/CD_3CN$ 50/50 (bottom three spectra).

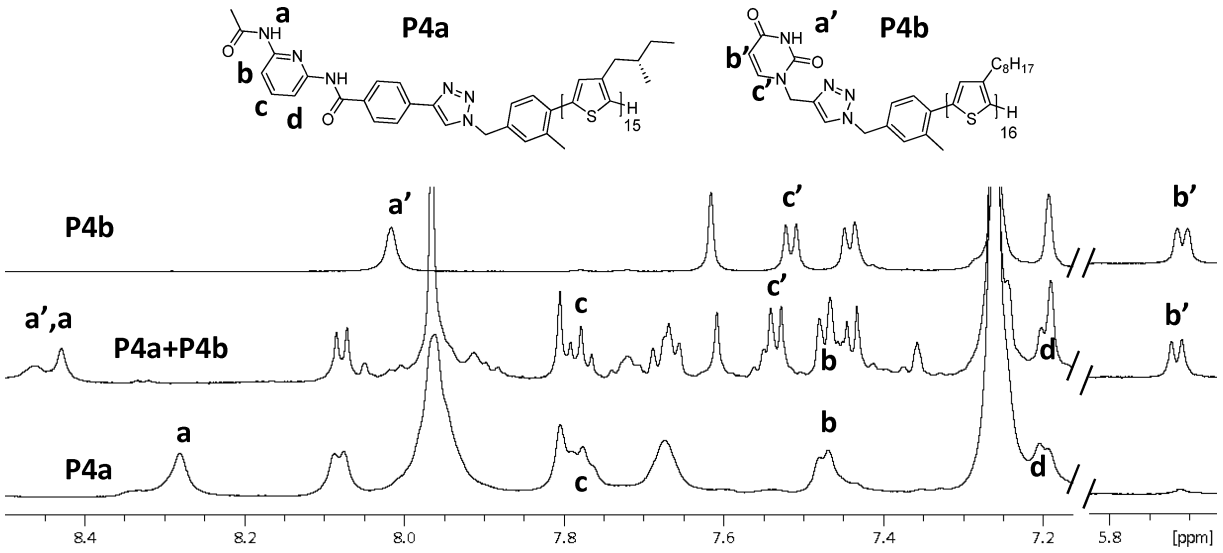

Figure 7. ^{1}H NMR of **P4a**, **P4b**, and **P4a** and **P4b** mixed in equimolar amounts in $CDCl_3$.

of **P4a** and **P4b**. In order to ensure reproducibility, the nonsolvent was added slowly by a syringe pump (0.5 mL/min). After the addition of the different nonsolvent amounts, CD and UV−vis spectra were measured. Upon analyzing the CD results (Figure 8) of the chiral **P4a** and the equimolar mixture of **P4a** and **P4b**, it is obvious that the chiral expression of the mixture is lower than the response of pure **P4a**. Important to note here is that the results are presented in g/L **P4a** used in the experiment. This allows a direct comparison of the chiral expression of the mixture and **P4a**. This shows that the H-bond formation reduces the chiral stacking to about 35% of the original chiral response by the presence of the achiral **P4b** in the mixture. When considering the UV−vis spectra of both **P4a** and **P4b** (Figure 8 and Figure S22, respectively), the polymer chains of **P4b** start to stack at lower amounts of CH_3CN than in the case of **P4a** (42% versus 58%, respectively). Previous research has shown that, for a block copolymer composed of blocks which differ more than 2C's in the length of the side chain, the blocks tend to microphase separate.[38] Taking a difference in side chain length (8C's compared to 4C's) of both monomer units in the mixture of **P4a** and **P4b** into account, a microphase separation can be expected. It is also been shown that the block that aggregates first dictates or influences the stacking behavior (chiral or achiral) of the block that aggregates later on (first come, first served principle[46]). Since the achiral block self-assembles first, these experiments suggest that this principle is also present in this supramolecular block copolymer.

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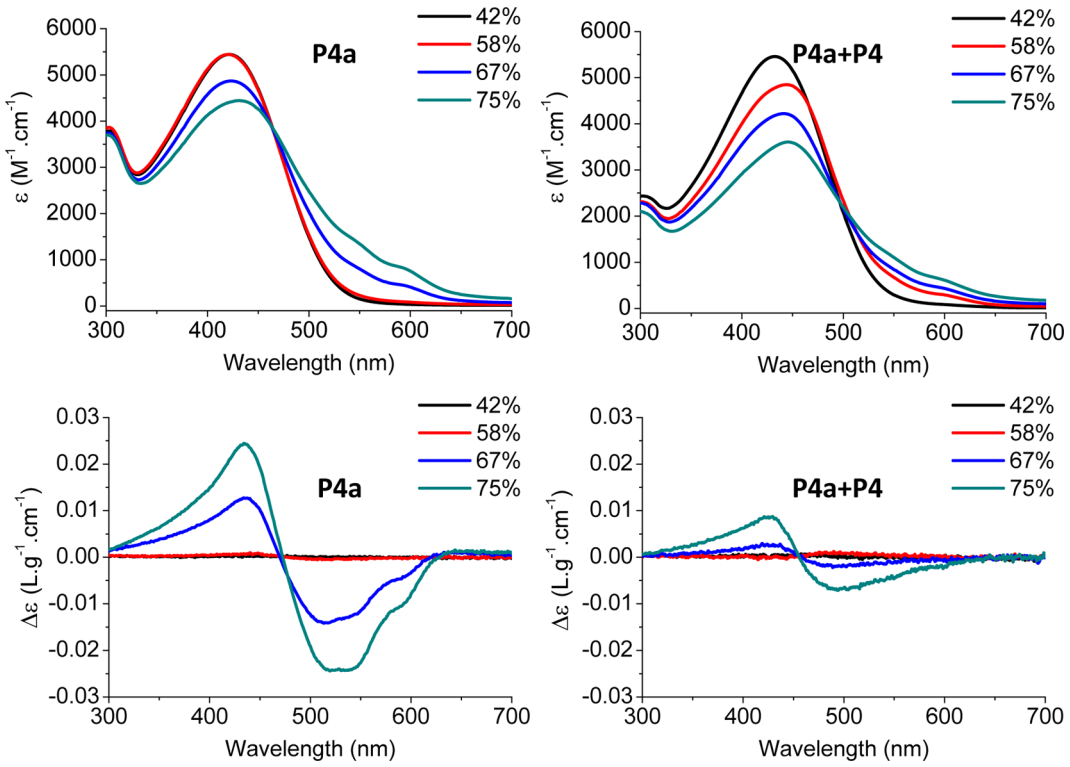

Figure 8. UV−vis (top) and CD (bottom) spectra in $CHCl_3$ and added amount (%) of CH_3CN of **P4a** (c_{start} = 0.025 g/L) (left) and the equimolar mixture **P4a** (c_{start} = 0.011 g/L) and **P4b** (c_{start} = 0.014 g/L) (right), $\Delta\varepsilon$ is expressed in L g^{-1} cm^{-1}; g L^{-1} is the mass concentration of **P4b**.

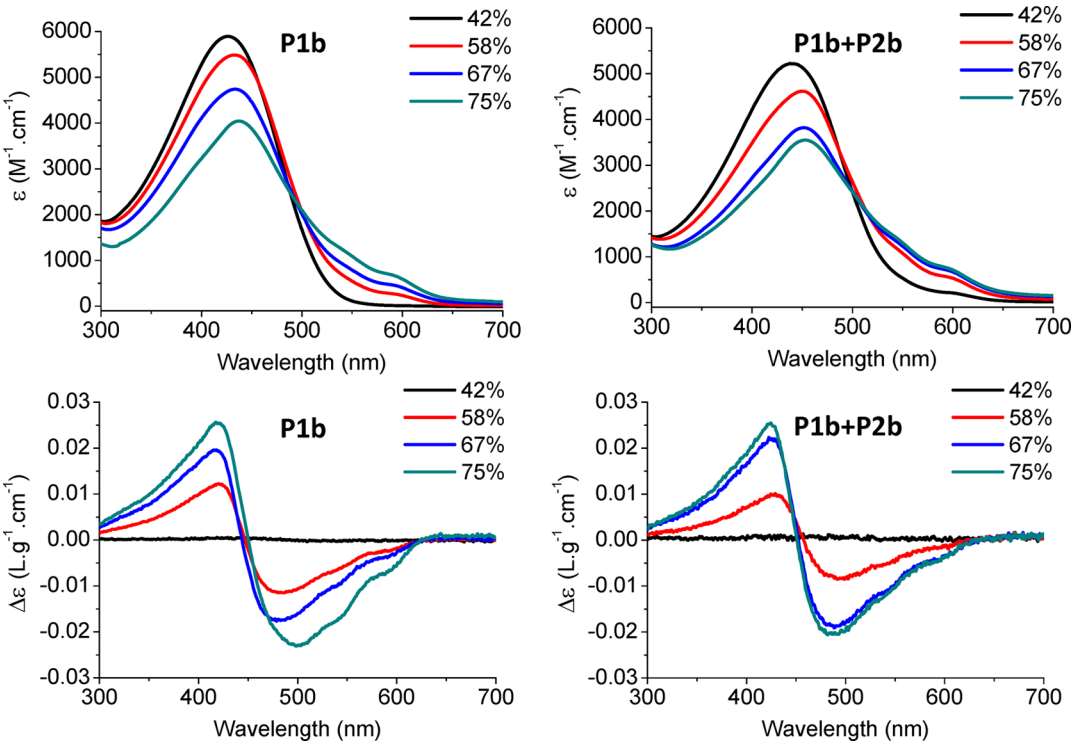

Figure 9. UV−vis (top) and CD (bottom) spectra in $CHCl_3$ and added amount (%) of CH_3CN of **P2a** (c_{start} = 0.025 g/L) (left) and the equimolar mixture **P2a** (c_{start} = 0.011 g/L) + **P2b** (c_{start} = 0.014 g/L) (right). $\Delta\varepsilon$ is expressed in L g^{-1} cm^{-1}; g L^{-1} is the mass concentration of **P2a**.

In order to prove that the reduction of $\Delta\varepsilon$ is indeed originating from the H-bond formation and the effect of the achiral block (**P4b**) on the chiral block (**P4a**) and not from the formation of some sort of mixed aggregates of both blocks, the experiment is repeated using **P2a**, **P2b**, and an equimolar mixture of both. These polymers are equipped with an alcohol function and are not able to from the H-bonds. The UV−vis experiments confirm that **P2b** (Figure S22) aggregates at lower amounts of CH_3CN compared to **P2a** (Figure 9, as was also the case for **P4a** and **P4b**). If the formation of mixed aggregates is

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the basis for the quenching of the chirality, the same reduction of chirality must be observed for the mixture compared to **P2a**. In contrast, if the two polymers self-assemble separately, the CD spectra will not be affected. The CD results for different amounts for CH_3CN are depicted in Figure 9. The CD spectra of the mixture and **P2a** are clearly similar, and no reduction of chiral expression is observed. Therefore, it can be concluded that H-bonds are formed between the two polymers and that this H-bond formation results in a quenching effect of the chiral response.

CONCLUSION

In conclusion, we succeeded in preparing functionalized P3ATs with a complete functionalization and control over polymerization. Through the use of postpolymerization reaction and click chemistry procedures, H-donor and -acceptor entities were attached to the end of the polymer chain, as confirmed by MALDI-ToF and ^{1}H NMR analysis. The interaction between the H-donor and -acceptor entities was monitored by the use of ^{1}H NMR in different solvents, proving the formation of a supramolecular all-conjugated diblock copolymers. The influence of the H-bonds on the aggregation behavior was studied using UV−vis and CD spectroscopy, and it was found that the chiral expression was partially quenched due to the achiral self-assembling of the **P4b** polymers. Because of the formation of the H-bonds and based on the fact that the achiral block stacks as first, the achiral aggregation behavior of the **P4b** block was also transferred to the chiral **P4a** block, following the "first come, first served principle".

ASSOCIATED CONTENT

Supporting Information

Experimental procedures, ^{1}H NMR and ^{13}C NMR of all new compounds; GPC data, ^{1}H NMR, FT-IR, and MALDI-ToF spectra of the polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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