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# Fulvenyl-Functionalized Polyisocyanides: Cross-Conjugated **Electrochromic Polymers with Variable Optical and Electrochemical Properties**

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**S** Supporting Information

ABSTRACT: We describe the preparation of arylisocyanide monomers bearing conjugated fulvenyl groups derived from 9benzylidene-9H-fluorene (Flu), 5-benzylidene-1,2,3,4tetraphenylcyclopentadiene (TPCp), and 5-benzylidene-5Hdibenzo[a,d]cycloheptene (Dbs). The electrochemical and optical properties of the monomers and their precursors have been characterized and consistently showed the effect of the conjugation of the respective functional group  $(-NO_2, -NH_2)$ -NHCHO, and  $-N \equiv C$ ) with the fulvenyl moiety. The isocyanides have been subsequently polymerized to the corresponding polyisocyanides (PICs), which exhibited



number-average molecular weights of 124-136 kDa (PDI = 2.0-2.7), as determined by gel permeation chromatography in THF vs polystyrene standards. The thermal, optical, and electrochemical properties of the polymers have been studied in detail. Spectroelectrochemical analyses of polymers equipped with redox-active pentafulvene groups show reversible electrochromism, which allows to lower the optical gap from 2.38 to 1.20 eV (Flu) and from 2.27 to 1.55 eV (TPCp) via chemical or electrochemical reduction.

# INTRODUCTION

The chemistry of tria-, penta-, and heptafulvenes<sup>1-15</sup> and fulvalenes<sup>4,11,16-21</sup> (Figure 1A), their synthetic preparation, and the study of their physical properties have been the subject of continuous interest throughout the past decades. These nonalternant hydrocarbons do not exhibit classic Hückel aromaticity but can form ionic species upon reduction (pentafulvenes) or oxidation (tria- and heptafulvenes) that experience substantial aromatic stabilization via cyclic delocalization. Pentafulvenes in particular have attracted growing interest due to their potential use as electron accepting (ntype) component in organic electronic applications. Extensive efforts have been made to broaden their synthetic accessibility<sup>22-26</sup> and to tailor their optical absorption properties and accessible redox potentials. For instance, the electron affinities of the 6,6-dicyanopentafulvenes (2, Figure 1B)<sup>27-32</sup> can be broadly varied via the substitution pattern on the fivemembered ring, while the compounds can be reversibly reduced at electrochemical potentials in the suitable range for organic n-type acceptor materials of -3.5 to -4.0 eV.<sup>33</sup> The potentialities of this class of substances were demonstrated by Wudl,<sup>34</sup> who reported the benzannulated pentafulvalene 1 (Figure 1B). 1 can be reversibly reduced to its radical anion  $1^{-\bullet}$  at  $E_{1/2}^{\text{red1}} \approx -1.2$  V, relative to the ferrocene/ferrocenium redox couple (FcH/FcH<sup>+</sup>),<sup>35,36</sup> corresponding to an electron affinity of ca. -3.9 eV, and could be successfully employed as

electron acceptor in organic photovoltaic cells. Applications of hepta- and triafulvene-derived compounds have been investigated much less comprehensively. Heptafulvalenes can serve as chemical sensors that exhibit turn-on fluorescence.<sup>37,38</sup> However, the investigation of hepta- and triafulvenes as electron-donating (p-type) materials seems limited by their lower redox stability. For instance, dibenzo [a,d] heptafulvenes (3, Figure 1B) exhibit only irreversible oxidation between +0.1 V  $(R = NMe_2)^{39}$  and +0.85 V (R = H).<sup>40</sup> A reversible first oxidation can be observed for tetraphenyltriafulvene (4,  $E_{ox}$  = +0.3 V, Figure 1B),<sup>41</sup> while donor-stabilized 2,3-diaminotriafulvenes are much more redox stable, but at the expense of a significantly lower oxidation potential ( $E_{ox} \approx -0.14 \text{ V}^{42,43}$ ). Because of the variable electronic properties cited above, polyfulvenes linked via carbon atoms of the ring have been proposed as a versatile class of electronic materials.<sup>44</sup> However, none of the suggested polymers could so far be prepared. In this paper, we report the first examples of compounds that formally represent polyfulvenes linked via the exocyclic fulvene double bond. To achieve this goal, we aimed at combining the electronic properties of fulvenes with those polyisocyanides<sup>45–48</sup> (PIC, Figure 1C,D).

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Figure 1. (A) Basic structures of fulvenes and fulvalenes. (B) Examples for fulvalenes (1) and fulvenes (2–4) and their corresponding reduction and oxidation potentials relative to FcH/FcH<sup>+</sup>. (r)/(i): reversible/irreversible process. (C) Isocyanides and polyisocyanides. (D) Polymer structures targeted herein.

PICs have been investigated extensively since the 1970s<sup>45–48</sup> but have attracted renewed interest with the recent development of new polymerization catalysts that allow the living polymerization of isocyanides.<sup>49-52</sup> This has opened an access to the preparation of a variety of block copolymers including PICs as coblocks to conjugated polymers.<sup>53-59</sup> Still, reports of PICs as electronic materials are comparatively rare and focus on the introduction of functional side chains, rather on taking advantage of the electronic properties of the polymer backbone. The backbone of PICs consists of consecutive sp<sup>2</sup>hybridized imine-carbon atoms. However, the polymer structure is such that the carbon atoms within the main chain are linked by single bonds and are therefore crossconjugated. As a consequence, electronic effects typically associated with extended conjugation are not observed, as evidenced by comparatively large optical bandgaps of ca. 2.5 eV for poly(arylisocyanide)s.<sup>60,61</sup> However, reduction or oxidation of PICs bearing conjugated fulvenyl side-chains should lead to charged rings in the side-chains stabilized by aromatic delocalization and to concurrent redistribution of the  $\pi$ -electrons in the conjugated linker and the polymer backbone (Figure 2A,B). This redistribution constitutes a transformation



**Figure 2.** Examples for the redox response in a (A) pentafulvenyl- and (B) heptafulvenyl-functionalized PIC.

of the cross-conjugated polymer backbone into a more effectively conjugated polyacetylene-like system, which should exhibit a reduced optical gap.<sup>62-65</sup> This concept would be applicable to electron-accepting pentafulvenes (Figure 2A) and electron donating tria- or heptafulvenes (Figure 2B). This would make a class of electrochromic polymers available that cover a broad range of redox potentials and may be employed as cathode/anode materials in organic polymer batteries (OPBs)<sup>66,67</sup> and electrochromic applications.<sup>68-72</sup> PICs<sup>73-75</sup> and polyacetylenes<sup>62</sup> equipped with redox-active

PICs<sup>73–75</sup> and polyacetylenes<sup>62</sup> equipped with redox-active functional groups, which showed reversible electrochromic behavior, have been reported in the past. In these cases, however, the redox-active functional groups were not conjugated to the polymer backbone, and the accessible redox potentials were limited to those of the introduced ferrocenyl<sup>73,62</sup> and tetrathiafulvalenyl groups.<sup>74,75</sup>

The chemistry of isocyanides is well-developed, since alkyl and aryl isocyanides are commonly employed in organic syntheses<sup>76–79</sup> and as ligands in organometallic coordination chemistry.<sup>80–83</sup> The latter field is attracting growing attention due to emerging new applications of isocyano complexes as catalysts for hydration<sup>84</sup> and hydroarylation<sup>85,86</sup> and as luminophores and photosensitizers in photocatalysis<sup>87–95</sup> and materials chemistry.<sup>96</sup>

However, comparatively few examples are known, wherein isocyanide groups are conjugated to more extended  $\pi$ -systems. Examples of  $\alpha,\beta$ -unsaturated isocyanides<sup>97–104</sup> and very sensitive isocyanoimines<sup>105,106</sup> have been reported as well as diisocyano-oligophenylenes.<sup>87–95,107,108</sup> The limited number of examples prompted the questions of whether the targeted monomers would be synthetically accessible and whether subsequent polymerization would leave the fulvene moieties intact. In the following, we summarize our results on the preparation and study of a series of isocyanide monomers and the corresponding polymers.

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Scheme 1. (A) Synthetic Route for the Preparation of Isocyanide Monomers and Polyisocyanides<sup>a</sup> and (B) Introduced Fulvenyl Groups



<sup>*a*</sup>Reagents and conditions: (i) base, toluene/THF,  $-35 \text{ }^{\circ}\text{C} \rightarrow \text{RT}$ ; (ii) SnCl<sub>2</sub>, HCl, 70 °C; (iii) CHCl<sub>3</sub>, KOH, EtOH, [Et<sub>3</sub>NBz]<sup>+</sup>Cl, DCM, RT; (iv) 4-nitrophenylformate, THF, RT; (v) POCl<sub>3</sub>, DIPA, DCM; (vi) Ni[*o*-anisyl(dppe)]Br, toluene, RT.

#### RESULTS AND DISCUSSION

**Synthesis.** To explore this chemistry, we endeavored to prepare the polyisocyanides 12a-e depicted in Scheme 1B (a:  $R_m = 9$ -fluorenyl, Flu; b:  $R_m = 5$ -(1,2,3,4-tetraphenyl)-cyclopentadienyl, TPCp; c:  $R_m = 5$ -dibenzo[a,d]cycloheptenyl = dibenzo[a,d]suberenyl, Dbs; d:  $R_m = (2,5$ -dimethyl-3,4-diphenyl)cyclopentadienyl, MPCp; e:  $R_m = 2,3$ -dimesityl-cyclopropenyl, Cyp) that feature redox-active fulvenyl groups conjugated to the polymer backbone via a *p*-phenylene linker.

The corresponding isocyanide monomers (11) were synthesized from *p*-nitrophenyl-substituted fulvenes (Scheme 1, 8a-d), as outlined in Scheme 1. Fulvene 8a was prepared by Wittig coupling of the 9-fluorenyltriphenylphosphonium salt 7a with p-nitrobenzaldehyde. This approach proved impractical, however, for the preparation of the fulvenes 8b-d, which were instead synthesized by Wittig coupling of a tri(nbutyl)phosphonium salt (5) to 2,3,4,5-tetraphenylcyclopentadienone (6b), dibenzo[a,d]cyclohepten-5-one (6c), and 2,5-dimethyl-3,4-diphenylcyclopentadienone (6d), respectively. The use of electron-rich trialkylphosphonium salt 5 proved essential to effect conversion of these less reactive and sterically hindered ketones.<sup>109</sup> Interestingly, **6d** readily dimerizes to  $6d_2$  (Figure 3A) via [4 + 2]-cycloaddition but is in equilibrium with its monomer<sup>31,110</sup> and can therefore still be converted into the fulvene 8d. However, subsequent reduction of 8d to the corresponding aniline 9d failed under various conditions, and the synthesis of the corresponding isocyanide 11d was therefore not completed. Similarly, Wittig coupling of 2,3-dimesitylcyclopropenone (6e) with 5 furnished only trace amounts of the triafulvene 8e, which could not be isolated. Nevertheless, single crystals suitable for X-ray diffraction could be obtained of both the dimerization product  $6d_2$  (Figure 3A) and of the cyclopropenone 6e (Figure 3B1,B2). Crystal



Figure 3. (A) Crystal structure and valence structure of dimer  $6d_2$ , 2*R*,3*R*,3a*S*,4*S*,7*R*,7a*R*-diastereomer shown. (B1, B2) Crystal structure of 2,3-dimesitylcyclopropenone (top-down and side view). Ellipsoids drawn at 55% probability level. Hydrogen atoms have been omitted for clarity.

structures were also obtained for the successfully prepared p-nitrophenylfulvenes 8a-d and will be discussed in a subsequent section. The corresponding structural data has been enclosed in the Supporting Information.

In the next step, the *p*-nitro groups in **8a**–**c** were reduced with  $\text{SnCl}_2/\text{HCl}$  to give the corresponding anilines, from which the isocyanides were then synthesized via two different methods: Direct carbamylation<sup>77</sup> of the anilines with chloroform and concentrated sodium hydroxide solution was possible under phase transfer conditions. However, while this procedure provided high yields it proved difficult to reproduce and to scale up. Alternatively, formylation of the anilines with the *p*-nitrophenylformate<sup>111</sup> allowed to isolate the corresponding *N*-formamides **10a**–**c** in satisfying yields of 60–70%. Subsequent dehydration with POCl<sub>3</sub> and diisopropyl-

ethylamine (DIPA) then readily furnished the isocyanides 11a-c in yields of 75–95%.

The intermediates and the isocyanide monomers 11a-c were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and high-resolution mass spectrometry. The isocyanides **11a**, **11b**, and **11c** were unambiguously identified by their <sup>13</sup>C NMR resonances of the isocyanide carbon atom at 164.9, 165.3, and 162.8 ppm and their characteristic infrared absorption bands at 2119, 2118, and 2121 cm<sup>-1</sup>, respectively (see Figures S36, S39, and S41). Furthermore, reaction of the monomers with chloro(dimethyl sulfide)gold(I) (Me<sub>2</sub>S-Au(I)Cl) led to a signal shift of the isocyano bands in the infrared spectra to 2213, 2212, and 2214 cm<sup>-1</sup> (see Figures S36, S39, and S41), respectively, within the typical range for gold(I) complexes of isocyanides.<sup>112,113</sup>

**Structure and Properties of Conjugated Fulvenes.** In order to further elucidate the effects the variation of the fulvenyl moiety and the conjugated functional group  $(-NO_2, -NH_2, -NHCHO, \text{ and } -N \equiv C)$  on the electronic properties of the conjugated systems, the precursors and monomers have been investigated by UV-vis spectroscopy and electrochemical methods.

As exemplified in Figure 4, conjugation in the neutral fulvene structure without formal charges ( $\mathbb{R}^0$ , Figure 4, center)



**Figure 4.** Exemplary resonance structures. FG = functional group:  $-NO_{2^{j}} - NH_{2^{j}} - NHCHO$ , and  $-N \equiv C$ .

can lead to charge redistribution toward the fulvene moiety ( $\mathbb{R}^0 \leftrightarrow \mathbb{R}^-$ ) or toward the functional group ( $\mathbb{R}^0 \leftrightarrow \mathbb{R}^+$ ). This effect is expected to be most pronounced in donor–acceptor (D–A) systems and should lead to a more red-shifted optical

Table 1. Physicochemical Data of Substituted Fulvenes

absorption compared to analogous but mismatched donor– donor (D–D) or acceptor–acceptor (A–A) systems.

The UV-vis spectra of the fulvenes show absorption maxima in the range of 325-406 nm that largely reflect the properties of the respective combination of functional groups (Table 1 and Figure 5; see also Figures S1-S11). The trend is most pronounced in the amino-substituted derivatives 9a-cand in the amides 10a-c. The aniline 9b, featuring the strongest pentafulvene acceptor, exhibits the longest wavelength absorption with a maximum at  $\lambda_{max} = 406$  nm, and the lowest optical gap of  $E_{g}^{opt} = 2.56$  eV, followed by 9a ( $\lambda_{max} = 372$  nm,  $E_{g}^{opt} = 2.84$  eV). 9c exhibits a wider optical gap and a blue-shifted  $\lambda_{max}$  ( $\lambda_{max}$  = 325 nm (sh),  $E_g^{opt}$  = 3.35 eV; for deconvolution see Figure S9), which can be attributed to the donor-donor combination in this system. The amides show an analogous trend, with the TPCp derivative 10b ( $\lambda_{max} = 364$ nm,  $E_{g}^{opt} = 2.95 \text{ eV}$ ) exhibiting the most red-shifted absorption and the lowest optical gap, followed by the fluorenyl derivative **10a** ( $\lambda_{max} = 344$  nm,  $E_g^{opt} = 3.07$  eV). The Dbs-functionalized **10c** ( $\lambda_{max} = 318$  nm (sh),  $E_g^{opt} = 3.48$  eV, for deconvolution see Figure S10) again shows a widened optical gap. The blueshifted absorption and the wider optical gaps of the amides directly reflect the reduced donor strength of the Nformylamido compared to the amino groups.  $\overset{{\rm I}14,115}{}$  The same trend of the optical gaps and longest wavelength absorption maxima is observed for the monomers 11a-c (11a:  $\lambda_{max} = 336$ nm,  $E_g^{opt} = 3.04 \text{ eV}$ ; 11b:  $\lambda_{max} = 348 \text{ nm}$ ,  $E_g^{opt} = 2.82 \text{ eV}$ ; 11c:  $\lambda_{max} = 320 \text{ nm}$  (sh), and  $E_g^{opt} = 3.30 \text{ eV}$ ; for deconvolution see Figure S11). The low optical gap of 11b and the large gap of 11c are somewhat curious, however, since the isocyano group is a relatively strong acceptor, comparable to an acyl group,<sup>114,115</sup> and 11b and 11c therefore constitute A-A and D-A systems, respectively. We tentatively attribute this observation to the optical absorption in 11b being dominated by the properties of the fulvene moiety, while steric strain hinders effective conjugation in 11c. The strain in Dbs derivatives like 11c is evident from the crystal structure of 8c, wherein the nitrophenyl moiety is twisted out of the ring plane, even though an even stronger acceptor is present in this compound than in 11c (see Figure 8C1,C2 and associated

			UV-vis a	bsorption		electrochemical properties		
	mp [°C]	$\lambda_2 [nm]$	$\lambda_{ m max}$	$\lambda_{\rm onset}/E_{\rm g}^{\rm opt}$ b	[nm]/[eV]	$E_{1/2}^{c}$ [V]	$E_{\rm p}^{d}$ [V]	
8a	167.6-168.8		359	427	2.90	-1.43, -1.68		
8b	227.7-229.3	267	352	415	2.99	-1.52	-1.51, -1.59	
8c	152.3-153.1	289 <sup>a</sup>	360 <sup>a</sup>	422	2.94	-1.75	-1.79	
8d	185.9-187.4	269	341	415	2.99	-1.50, -1.70	-1.52, -1.68	
9a	oil		372	436	2.84			
9b	116.7-119.6	265	406	484	2.56			
9c	58.8-60.5	298 <sup>a</sup>	325 <sup>a</sup>	370	3.35	$+0.37, +0.52^{e}$		
10a	182.6-186.5		344	404	3.07			
10b	190.7-193.5	261	364	420	2.95			
10c	115.4-117.2	292 <sup>a</sup>	318 <sup>a</sup>	356	3.48			
11a	123.4-125.2		336	408	3.04	-1.93, -2.17		
11b	259.8–269.7 (dec)		348	440	2.82	-1.85, -2.28	-1.90, -2.29	
11c	152.2–160.4 (dec)	292 <sup>a</sup>	320 <sup>a</sup>	376	3.30	$+0.84, +0.97, +1.14^{e}$	$+0.80, +0.91, +1.11^{e}$	

<sup>*a*</sup>Shoulder band,  $\lambda_{max}$  derived via Gaussian deconvolution of the absorption spectrum. <sup>*b*</sup>Derived from the absorption onset of spectra recorded in CH<sub>2</sub>Cl<sub>2</sub> solution. <sup>*c*</sup>Half-potentials of reversible redox processes determined via cyclic voltammetry (CV) in THF (reduction) or CH<sub>2</sub>Cl<sub>2</sub> (oxidation) solution with 0.1 M [NnBu<sub>4</sub>][PF<sub>6</sub>] as supporting electrolyte. <sup>*d*</sup>Peak potentials determined via square-wave voltammetry (SWV) in THF (reduction) or CH<sub>2</sub>Cl<sub>2</sub> (oxidation) solution with 0.1 M [NnBu<sub>4</sub>][PF<sub>6</sub>]. <sup>*e*</sup>Peak potentials of irreversible oxidation.



Figure 5. UV-vis absorption spectra of isocyanide monomers and the corresponding precursors. Recorded in CH<sub>2</sub>Cl<sub>2</sub> solution.



Figure 6. Cyclic voltammograms of fulvenes and polyisocyanides. (A) 8a, 11a, and 12a. (B) 8b, 11b, and 12b. (C) 8c, 11c, and 12c. Black line: -NO<sub>2</sub>; red line: -NC; blue line: PIC.

comments). The optical properties of the nitro derivatives are similarly ambiguous. A–A-substituted fulvenes **8b** and **8d** exhibit comparatively large optical gaps of  $E_g^{opt} = 2.99 \text{ eV}$  each  $(\lambda_{onset} = 415 \text{ nm})$ , whereas for **8a**  $(\lambda_{onset} = 427 \text{ nm}, E_g^{opt} = 2.90 \text{ eV})$  and **8c**  $(\lambda_{onset} = 422 \text{ nm}, E_g^{opt} = 2.94 \text{ eV})$  lower optical gaps are observed. Seemingly, the properties of **8a** are dominated by the nitro group, while the formally electron-donating Dbs group is again not effectively conjugated to the acceptor.

Overall, we can say that the optical properties reflect electronic communication between the fulvenyl moiety and the peripheral functional groups, particularly when electron donors are present and donor—acceptor systems are created.

All compounds were nonfluorescent with the exception of **10b** and **11b**, which showed weak fluorescence in solution with

emission maxima at 431 and 470 nm, respectively (see Figure S5).

Analyses by cyclic voltammetry shows the *p*-nitrophenylfulvenes **8a**–**d** to undergo 2-fold reversible or quasi-reversible electrochemical reduction to the radical anion and dianion, respectively (Figure 6). The first reduction of **8a** occurs with a half-potential of  $E_{1/2}^{\text{red}1} = -1.43$  V vs FcH/FcH<sup>+</sup>, followed by a second reduction at  $E_{1/2}^{\text{red}2} = -1.68$  V. For **8b** one broad reduction wave centered on  $E_{1/2}^{\text{red}1} = -1.52$  V was observed, which could be resolved by square wave voltammetry (SWV) into two individual reductions at  $E_{p}^{\text{red}1} = -1.51$  V and  $E_{p}^{\text{red}2} =$ -1.59 V (see Figure S27). **8d** exhibited similar properties with  $E_{1/2}^{\text{red}1} = -1.50$  V and  $E_{1/2}^{\text{red}2} = -1.70$  V (see Figures S30 and S31). The donor-substituted **8c** showed only a broad, quasireversible reduction wave with an onset at ca. -1.45 V, which



Figure 7. (A) Resonance in p-nitrophenylfulvenes 8a-d upon electrochemical reduction. (B) Numbering of solid-state structures of 8a-d.



Figure 8. Crystal structures of *p*-nitrophenylfulvenes. Top-down and side views of 8a (A1, A2), 8b (B1, B2), 8c (C1, C2), and 8d (D1, D2). Ellipsoids drawn at 55% probability level. Hydrogen atoms have been omitted for clarity.

Table 2. Structural Data for *p*-Nitrophenylfulvenes (Numbering According to Figure 7B)

	XRD	C5–C6 [Å]	C4–C5 [Å]	C1–N [Å]	C3/C3'-C4-C5-C6 [deg]	C4-C5-C6-C7/C7' [deg]	C5-C6/ring plane [deg]
8a	P21/c, Z = 4	1.349(1)	1.517(1)	1.511(1)	59.9(1)/-122.8(1)	5.2(2)/-175.7(1)	1.4(1)
8b	P21/c, Z = 4	1.350(3)	1.476(3)	1.462(3)	52.1(2)/-128.5(2)	7.8(3)/-173.9(2)	0.4(1)
8c	P21/c, Z = 4	1.340(2)	1.474(2)	1.468(2)	30.9(2)/-151.3(1)	5.9(2)/-178.6(1)	50.6(1)(1)
8d	P21/c, Z = 4	1.356(1)	1.468(1)	1.469(1)	34.4(2)/-149.8(1)	5.4(2)/-179.6(1)	4.1(1)

could not be resolved further by SWV ( $E_p^{red} = -1.79$  V, see Figure S28). No further reduction processes were observed down to -2.5 V. The first reductions generally occur close to the reduction potential of common nitroarenes (4-nitrobiphenyl: -1.43 V/-2.00 V; 4-nitro-1,2,3,6,7,8-hexahydropyrene: -1.62 V/-2.13 V<sup>116</sup>), while the potential of second reduction scales with the acceptor strength of the fulvene moiety. We can therefore conclude that the first electron reduction mainly involves the nitrophenyl ring, while the second reduction is governed by the fulvene moiety (Figure 7A).

For the isocyanides **11a** and **11b** two steps of irreversible electrochemical reduction could also be observed (Figure 6). In agreement with the weaker electron-withdrawing effect of the isocyanide group,<sup>114,115</sup> the first and second reduction potentials each appeared shifted by 0.40-0.45 V to lower potential compared to the nitro compounds.

Electrochemical oxidation potentials of 9c and 11c were also measured. For the electron-rich aniline 9c two oxidations with peak potentials at +0.37 and +0.52 V vs FcH/FcH<sup>+</sup> were observed, while monomer 11c exhibited three irreversible oxidation processes at higher potentials ( $E_p^{ox} = +0.84$ , +0.97, and +1.14 V vs FcH/FcH<sup>+</sup>), in agreement with the electronwithdrawing nature of the isocyano group.

The available crystal data on the series of *p*-nitrophenylfulvenes 8a-d (Figure 8 and Table 2; see Figure 7B for numbering), enabled us to evaluate the structural effects of

the conjugation between the nitro group and the fulvene moieties. The most relevant parameter in this respect is the fulvene bond (C5–C6). For 8a, 8b, and 8d these bonds are of comparable length (8a: 1.349(1) Å; 8b: 1.350(3) Å; 8d: 1.356(1) Å) and indicate no significant weakening of the bond through resonance, in agreement with the acceptor-acceptor character of these systems. However, the C5-C6 bond in the Dbs-containing fulvene 8c (1.340(2) Å) is marginally shorter than in the pentafulvenes-even though resonance should be more effective in this donor-acceptor system. The reason lies in the deformation of the central ring in 8c into a boat conformation that leads to the C5-C6 fulvene bond being twisted out of the mean plane of the seven-membered ring by  $50.6(1)^{\circ}$  (C2, Figure 8). Similar deformations have been previously observed in 4-methylenedibenzo[a,d]-cycloheptenes, <sup>117-119</sup> even in the presence of strong acceptors in the periphery,<sup>120</sup> which indicates that the fulvene bond is not effectively conjugated to the Dbs unit. In contrast, the fulvene moieties in 8a, 8b, and 8d are close to coplanar  $(\langle 4.1(1)^{\circ})$ , thus enabling effective conjugation with peripheral substituents. Unfortunately, the lack of effective conjugation in Dbs-based systems indicates that this molecular structure is not ideal for the applications targeted herein. Instead, triafulvenes or non-benzannulated heptafulvenes may be better suited as ptype materials.

**Polymer Syntheses and Properties.** Polymers 12a-c were prepared from solutions of the monomers in toluene

(11b,c) or in a toluene/THF solvent mixture (11a) by stirring overnight at room temperature in the presence of (*o*-anisyl)Ni(II)(dppe) bromide (dppe: 1,2-bisdiphenyl-phosphinoethane).<sup>121</sup> The polymers were isolated and purified by precipitation into hexanes, followed by centrifugation, which furnished orange (12a), brown (12b), and yellow (12c) powders. The polymers dissolved well in polar, halogenated, and aromatic organic solvents such as THF, dichloromethane, and toluene but remained insoluble e.g. in diethyl ether and acetonitrile.

Thermal analysis via thermal gravimetry (TGA) showed them to be thermally robust, with decomposition temperatures  $(T_d)$  of 345 °C for 12c and 365 and 370 °C for 12b and 12a, respectively (see Figure S44). Differential scanning calorimetry showed no melting or phase transitions prior to decomposition.

The formation of polyisocyanides could be confirmed by IR spectroscopy, which showed the typical C=N stretching bands around  $\tilde{\nu} = 1600 \text{ cm}^{-1}$  (see Figures S37, S40, and S42).<sup>122–124</sup> The polymers exhibited number-average molecule weights of  $M_{\rm p} = 136-124$  kDa, as determined via gel permeation chromatography in THF, relative to polystyrene standards, and showed polydispersities of 2.0-2.7 (see Figure \$32). The polymers were found to be stable in air both as solids and as spin-coated films as well as in dry solvents under an inert atmosphere. Slow decomposition occurred, however, in solutions exposed to air and moisture. We attribute this to partial hydrolyses of the imine groups on the polyisocyanides backbone, as indicated in Scheme 2, which is signified by the emergence of a carbonyl stretching vibration in IR spectra (see Figure S38 and associated comments in the Supporting Information).





**Mass Spectrometry.** Given that polyisocyanides are rodlike polymers, the molecular weights derived from GPC most likely overestimate the actual molecular weights of the material. To further corroborate the polymer formation, **12a** and **12b** were therefore also analyzed by matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry (see Figures S33 and S34), which has only rarely been employed to characterize polyisocyanides.<sup>125</sup> In both cases, signal series up to ca. 8 kDa, which correspond to more than 25 and 15 repeat units for **12a** and **12b**, respectively, could be observed via linear mode MALDI-TOF MS. The observed mass range is significantly lower than

the molecular weights derived from GPC. We attribute this difference to fragmentation of the high-molecular-weight chains upon ionization, which is not unusual in MALDI-MS,<sup>126,127</sup> and more facile ionization of these lower molecular weight fragments. This assumption is corroborated by data of a reference sample of poly(*p*-methoxyphenylisocyanide) ( $M_n$  = 5.3 kDa, PDI = 1.45), which showed a signal distribution that matched the GPC data (see Figure S35 and associated comments in the Supporting Information).

Information about the polymer chain ends could not be derived from the available data due to the lower resolution of linear mode MALDI-TOF-MS and also due to the large number of possible end-groups that are generated by different initiation pathways, fragmentation, and partial hydrolyses of individual imine bonds.

**Optical and Electrochemical Properties.** Compared to the monomers (**11a**:  $\lambda_{max} = 336$  nm; **11b**:  $\lambda_{max} = 348$  nm; **11c**:  $\lambda_{max} = 400$  nm, shoulder band), the polymers **12a**-c exhibit moderately red-shifted absorption maxima, with  $\lambda_{max}$  values in solution of 344 nm (**12a**), 368 nm (**12b**), and 400 nm (**12c**, shoulder band) (Figure 9) and also show only a slight



Figure 9. UV–vis absorption spectra of polyisocyanides in  $CH_2Cl_2$  solution and as thin films.

bathochromic shift, when moving from solution to thin films. However, both in solution and in the thin film, the absorption falls off gradually toward longer wavelengths, leading to significantly lowered optical gaps of 2.38 eV (12a), 2.27 eV (12b), and 2.40 eV (12c). In the case of 12c only a single broad absorption band centered on 400 nm can be discerned. However, for 12a and 12b the origin of these tailings can be linked to weaker underlying absorption bands centered on 420 nm (12a) and 500 nm (12b), respectively, which have been

Table 3. Physicochemical Properties of Polyisocyanides 12a-c

					UV-vis absorption					electrochemical properties <sup>c</sup>		
	$M_{\rm n}$ [kDa]	$DP_n$	PDI	$T_d^{a}$	$\lambda_{\max}^{sol}$ [nm]	$\lambda_{\mathrm{onset}}^{\mathrm{sol}}$ [nm]	$\lambda_{\max}^{\mathrm{film}}$ [nm]	$\lambda_{\mathrm{onset}}^{\mathrm{film}}$ [nm]	$E_{\rm g}^{ m opt}$ [nm]	$E_{\rm p}^{\rm CVd}$ [V]	$E_{\rm p}^{\rm SWVe}$ [V]	
12a	136	487	2.7	370	344	494	347 (420 <sup>b</sup> )	520	2.38	-2.44		
12b	132	273	2.0	365	368	520	$381 (500^{b})$	560	2.27	-1.55, -2.03	-1.50, -1.91	
12c	124	407	2.7	345	400 <sup>b</sup>	498	400 <sup>b</sup>	517	2.40	+1.02		

<sup>*a*</sup>Decomposition temperature determined by TGA. <sup>*b*</sup>Longest wavelength absorption band derived via Gaussian deconvolution of the absorption spectra. <sup>*c*</sup>Recorded as dip-coated film on a platinum electrode vs 0.1 M  $[NnBu_4][PF_6]$  in NCMe solution. <sup>*d*</sup>Peak potentials observed in cyclic voltammetry. <sup>*c*</sup>Peak potentials observed in square-wave voltammetry.



Figure 10. Spectroelectrochemical response of polyisocyanides to electrochemical reduction: (A) 12a and (B) 12b.

determined by Gaussian deconvolution of the thin film absorption spectra (see Figures S12–S17). Overall, the optical gaps of the polymers are smaller than in typical poly-(arylisocyanide)s, while the absorption maxima are observed in a similar range (e.g., poly(4-methoxyisocyanide):  $\lambda_{max} = 360$  nm,  $\lambda_{onset} = 490$  nm, and  $E_g^{opt} = 2.53$  eV;<sup>128</sup> see Figure S18).

Since the absorption maxima of the polymers lie in the same range as those of the molecular precursors, we attribute the observed main absorption bands to individual repeat units and functional groups. The significantly lowered optical gaps of the polymers compared to the monomers indicate extended conjugation in the polymers. However, analyses of polymer batches with different molecular weights showed no correlation between the degree of polymerization and the absorption spectra of the polymers, even for low-MW batches with  $DP_n <$ 10 (see Figures S2, S4, and S7). Conjugation along the polymer backbone therefore does not seem to substantially contribute to the overall absorption, likely because steric crowding of the PIC backbone leads to helical torsion angles between adjacent imine-groups (>35°).45-47 Notably, PICs can also adopt a syndio-conformation<sup>129</sup> wherein imine dyads assume a coplanar geometry (R–N=C–C=N–R:  $\approx 180^{\circ}$ ), while being rotated by ca.  $90^{\circ}$  relative to neighboring imine groups. We therefore tentatively attribute the lowered optical gaps to conjugation that largely involves adjacent repeat units, rather than extended conjugation along the polymer backbone.

Electrochemical characterization of the polymers also reflected the different peripheral substituents (Figure 6): Thin films of 12a showed irreversible reduction with an onset at -2.20 V vs FcH/FcH<sup>+</sup>. The reduction does not result in decomposition of the polymer, however, since the film remains redox-active and only gradually degrades over multiple redox cycles (see Figure S29). 12b showed a broad quasi-reversible reduction with an onset at -1.30 V vs FcH/FcH<sup>+</sup>, while for 12c only irreversible oxidation was observed to set in at +0.65 V vs FcH/FcH<sup>+</sup>. The cathodic shift of the reduction potentials of 12a and 12b, relative to the monomers, may be attributable to the lower electron-withdrawing character of the poly(imine) backbone compared to the isocyano group.<sup>114,115</sup> The irreversibility of the oxidation of 12c may be due to detachment of the polymer film from the electrode or due to degradation of the polymer. The latter is more likely, however, since its precursors also did not exhibit chemically reversible redox behavior. Notably, the reduction potential of 12b

corresponds to a LUMO level of ca. -3.8 eV, which renders this polymer suitable for use e.g. n-type acceptor in organic photovoltaics.<sup>35,36</sup>

**Spectroelectrochemical Analyses.** Nevertheless, the quasi-reversible redox behavior of 12a and 12b showed that these materials can serve as electrochromic materials. We therefore also studied the changes in their absorption spectra upon chemical  $(12a^{redC}/12b^{redC})$  and electrochemical  $(12a^{redE}/12b^{redE})$  reduction (see the Supporting Information for experimental details).

12a showed a strong electrochromic response with the emergence of a broad band centered on 700 nm, accompanied by a shift of the absorption onset from 550 nm  $(E_{\sigma}^{opt}(12a) =$ 2.25 eV)<sup>130</sup> to ca. 1030 nm  $(E_{\sigma}^{opt}(12a^{redE}) = 1.20 \text{ eV}, \text{ Figure})$ 10A). The absorption change sets in at -1.50 V vs FcH/FcH<sup>+</sup> and was found to be largely reversible, since reversal of the applied voltage lead to disappearance of the long wavelength band (see Figure S20). Partial degradation of the materials occurred, however, since the original baseline could not be fully recovered. We attribute this to the gradual degradation of the polymer, as observed in cyclic voltammetry experiments (see Figure S29). Virtually full reversibility was observed for polymer 12b (Figure 10B; see also Figures S21 and S22). Here, in agreement with the high electron affinity of the TPCp group, the electrochromic response already sets in at ca. -1.20V vs FcH/FcH<sup>+</sup>. A weakening of the main absorption band at 390 nm was observed, while two weaker bands centered on 480 and 540 nm emerge. The absorption onset shifts accordingly from 560 nm  $(E_g^{opt}(12b) = 2.21 \text{ eV})^{130}$  to ca. 800 nm  $(E_{\alpha}^{\text{opt}}(12\mathbf{b}^{\text{red}E}) = 1.55 \text{ eV})$ . Chemical reduction lead to similar results (Figures S23-S26): The absorption onset of 12a shifted to ca. 900 nm  $(E_g^{opt}(12a^{redC}) = 1.38 \text{ eV})$ , and the one of 12b shifted to  $\approx 1100 \text{ nm} (E_{\alpha}^{\text{opt}}(12b^{\text{red}C}) = 1.13 \text{ eV})$ . We attribute the different absorption shifts compared to electrochemical reduction to presence of stronger coordinating metal cations, instead of the noncoordinating  $nBu_4N^+$  counterions in the electrochemical experiments. Exposure of the chemically reduced polymers to air then resulted in dedoping (Figures S24 and S26) but lead to only partial recovery of the baseline, likely due to the harsher reaction conditions in these experiments and concurrent decomposition of the polymers.

The decrease of the optical gaps in electrochemical and chemical reductions of  $-1.05 \text{ eV} (12a \rightarrow 12a^{\text{red}E})$  and  $-0.87 \text{ eV} (12a \rightarrow 12a^{\text{red}C})$ , respectively, for 12a and of -0.66 eV

 $(12b \rightarrow 12b^{redE})$  and  $-1.08 \text{ eV} (12b \rightarrow 12b^{redC})$ , respectively, for 12b corroborates the concept laid out in the Introduction (Figure 2). However, whether newly emerging absorption bands originate from the switch of the electronic configuration in the main chain or from the charged side-chains could not be ascertained at this point.

# CONCLUSION

In summary, we have prepared a series of penta- and heptafulvene derivatives bearing conjugated nitro, amino, Nformylamino, and isocyanophenyl groups and characterized their optical, electrochemical, and structural properties. These analyses showed a clear correlation of the electronic properties between the introduced (electron-donating or -accepting) fulvene moiety and the respective functional group. Furthermore, we polymerized the respective fluorenyl-, tetraphenylcyclopentadienyl-, and dibenzo [a,d] cycloheptenylfunctionalized isocyanides (11a-c) to the corresponding polyisocyanides (12a-c). The polymers 12a-c were shown to be chemically robust materials with optical, electrochemical, and electrochromic properties governed by the redox-active fulvenyl groups. Furthermore, the tetraphenylcyclopentadienylfunctionalized polymer 12b exhibited a LUMO level of ca. -3.8 eV and may therefore serve as n-type material in a range of organic electronic applications. Most importantly, however, the large-bandgap polymers 12a and 12b ( $E_g^{opt} = 2.38$  and 2.27 eV) exhibit a largely reversible electrochromic response that allows the reduction of their optical gap by  $\Delta E_g^{opt} \approx -0.7$  to -1.1 eV, depending on the experimental conditions. The absorption properties of these polymers can therefore be switched from largely transparent to opaque across the whole visible range.

So far, we were not able to further elucidate the changes to electronic structure of the polymers upon reduction due to the sensitivity of the polymers in the reduced state. A more detailed determination of the origin of the changed absorption behavior will require the study of representative oligomeric model systems. Work toward this end is currently in progress in our group.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.8b00977.

Additional analytical data, detailed experimental proce-

dures, copies of spectra, and crystallographic data (PDF)

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#### Notes

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#### ABBREVIATIONS

Flu, 9-fluorenyl; TPCp, 5-(1,2,3,4-tetraphenyl)cyclopentadienyl; Dbs, 5-(dibenzo[a,d])cycloheptenyl, also referred to as 5-dibenzo[a,d]suberenyl; MPCp, 5-(1,4-dimethyl-2,3-diphenyl)cyclopentadienyl; Cyp, 2,3-dimesitylcyclopropenyl; GPC, gel permeation chromatography; TGA, thermal gravimetry; CV, cyclic voltammetry; SWV, squarewave voltammetry.

#### REFERENCES

(1) Preethalayam, P.; Krishnan, K. S.; Thulasi, S.; Chand, S. S.; Joseph, J.; Nair, V.; Jaroschik, F.; Radhakrishnan, K. V. Recent Advances in the Chemistry of Pentafulvenes. *Chem. Rev.* **2017**, *117*, 3930–3989.

(2) Neuenschwander, M. In *Fulvenes in Double-Bonded Functional Groups*; Patai, S., Ed.; John Wiley & Sons, Inc.: Chichester, UK, 1989; Vol. 2, Part 2.

(3) Bergmann, E. D. Fulvenes and Substituted Fulvenes. *Chem. Rev.* **1968**, *68*, 41–84.

(4) Haberland, S.; Finke, A. D.; Kerisit, N.; Katan, C.; Trolez, Y.; Gawel, P.; Leito, I.; Lokov, M.; Jaerviste, R.; Kaupmees, K.; Trapp, N.; Ruhlmann, L.; Boudon, C.; Himmel, D.; Diederich, F. Enhancement of Push-Pull Properties of Pentafulvene and Pentafulvalene Derivatives by Protonation at Carbon. *Eur. J. Org. Chem.* **2018**, 2018, 739–749.

(5) Kerisit, N.; Finke, A. D.; Trapp, N.; Leroux, Y. R.; Guillemin, J.-C.; Trolez, Y.; Diederich, F. New Reactivity of 6,6-Bis-donorsubstituted Pentafulvenes: One-step Synthesis of Highly Substituted [3]-Cumulene and Dihydropentalene. *Tetrahedron* **2015**, *71*, 4393– 4399.

(6) Mohamed, R. K.; Mondal, S.; Jorner, K.; Delgado, T. F.; Lobodin, V. V.; Ottosson, H.; Alabugin, I. V. The Missing  $C_1$ - $C_5$ Cycloisomerization Reaction: Triplet State Antiaromaticity Relief and Self-Terminating Photorelease of Formaldehyde for Synthesis of Fulvenes and Enynes. J. Am. Chem. Soc. **2015**, 137, 15441–15450.

(7) Shurdha, E.; Repasy, B. K.; Miller, H. A.; Dees, K.; Iacono, S. T.; Ball, D. W.; Balaich, G. J. Symmetrical Bis(fulvene) Chromophores: Model Compounds for Acceptor-Donor-Acceptor Dye Architectures. *RSC Adv.* **2014**, *4*, 41989–41992.

(8) Campolo, D.; Arif, T.; Borie, C.; Mouysset, D.; Vanthuyne, N.; Naubron, J.-V.; Bertrand, M. P.; Nechab, M. Double Transfer of Chirality in Organocopper-Mediated Bis(alkylating) Cycloisomerization of Enediynes. *Angew. Chem., Int. Ed.* **2014**, *53*, 3227–3231.

(9) Finke, A. D.; Haberland, S.; Schweizer, W. B.; Chen, P.; Diederich, F. A Mild, Thermal Pentafulvene-to-Benzene Rearrangement. *Angew. Chem., Int. Ed.* **2013**, *52*, 9827–9830.

(10) Jayamurugan, G.; Dumele, O.; Gisselbrecht, J.-P.; Boudon, C.; Schweizer, W. B.; Bernet, B.; Diederich, F. Expanding the Chemical Structure Space of Opto-Electronic Molecular Materials: Unprecedented Push-Pull-Chromophores by Reaction of a Donor-Substituted Tetracyanofulvene with Electroch-Rich Alkynes. J. Am. Chem. Soc. **2013**, 135, 3599–3606.

(11) Dahlstrand, C.; Rosenberg, M.; Kilså, K.; Ottosson, H. Exploration of the  $\pi$ -Electronic Structure of Singlet, Triplet, and Quintet States of Fulvenes and Fulvalenes Using the Electron Localization Function. *J. Phys. Chem. A* **2012**, *116*, 5008–5017.

(12) Rosenberg, M.; Ottosson, H.; Kilså, K. Influence of Excited State Aromaticity in the Lowest Excited Singlet State of Fulvene Derivatives. *Phys. Chem. Chem. Phys.* **2011**, *13*, 12912–12919.

(13) Dahlstrand, C.; Yamazaki, K.; Kilså, K.; Ottosson, H. Substituent Effects on the Electron Affinities and Ionization Energies of Tria-, Penta-, and Heptafulvenes: A Computational Investigation. J. Org. Chem. 2010, 75, 8060–8068. (14) Ottosson, H.; Kilså, K.; Chajara, K.; Piqueras, M. C.; Crespo, R.; Kato, H.; Muthas, D. Scope and Limitations of Baird's Theory on Triplet State Aromaticity: Application to the Tuning of Singlet-Triplet Energy Gaps in Fulvenes. *Chem. - Eur. J.* **2007**, *13*, 6998–7005.

(15) Godman, N. P.; Adas, S. K.; Hellwig, K. M.; Ball, D. W.; Balaich, G. J.; Iacono, S. T. Synthesis, Electrochemical Characterization, and Linear Free Energy Relationship of 1,3-Diphenyl-6-alkyl/ arylfulvenes. *J. Org. Chem.* **2016**, *81*, 9630–9638.

(16) Neuenschwander, M. Substituent Effects on the  $\pi$ -Bond Delocalization of Fulvenes and Fulvalenes. Are Fulvenes Aromatic? *Helv. Chim. Acta* **2015**, *98*, 763–784.

(17) Halton, B. The Fulvalenes. Eur. J. Org. Chem. 2005, 2005, 3391-3414.

(18) Neuenschwander, M. Synthetic and NMR-Spectroscopic Investigations of Fulvenes and Fulvalenes. *Pure Appl. Chem.* **1986**, *58*, *55–66*.

(19) Kinjo, R.; Ishida, Y.; Donnadieu, B.; Bertrand, G. Isolation of Bicyclopropenylidenes: Derivatives of the Smallest Member of the Fulvalene Family. *Angew. Chem., Int. Ed.* **2009**, *48*, 517–520.

(20) Piekarski, A. M.; Mills, N. S.; Yousef, A. Dianion and dication of tetrabenzo[5.7]fulvalene. Greater antiaromaticity than aromaticity in comparable systems. *J. Am. Chem. Soc.* **2008**, *130*, 14883–14890.

(21) Hu, B.; Lu, P.; Wang, Y. Fluorescent Chemosensors Based on 9-Cycloheptatrienylidene Fluorenes (9-CHFs). *New J. Chem.* 2013, 37, 1645–1653.

(22) Peloquin, A. J.; Stone, R. L.; Avila, S. E.; Rudico, E. R.; Horn, C. B.; Gardner, K. A.; Ball, D. W.; Johnson, J. E. B.; Iacono, S. T.; Balaich, G. J. Synthesis of 1,3-Diphenyl-6-alkyl/aryl-Substituted Fulvene Chromophores: Observation of  $\pi$ - $\pi$  Interactions in a 6-Pyrene-Substituted 1,3-Diphenylfulvene. J. Org. Chem. **2012**, 77, 6371-6376.

(23) Aqad, E.; Leriche, P.; Mabon, G.; Gorgues, A.; Khodorkovsky, V. Novel D- $\pi$ -A Chromophores Based on the Fulvene Accepting Moiety. *Org. Lett.* **2001**, *3*, 2329–2332.

(24) Kondo, K.; Goda, H.; Takemoto, K.; Aso, H.; Sasaki, T.; Kawakami, K.; Yoshida, H.; Yoshida, J. Micro- and Macro-scopic Second-order Non-linear Optical Properties of Fulvene Compounds. *J. Mater. Chem.* **1992**, *2*, 1097–1102.

(25) Dane, E. L.; Swager, T. M. Carbanionic Route to Electroactive Carbon-Centered Anion and Radical Oligomers. *Org. Lett.* **2010**, *12*, 4324–4327.

(26) Chajara, K.; Ottosson, H. An Improved Pathway to 6,6-Disubstituted Fulvenes. *Tetrahedron Lett.* **2004**, *45*, 6741–6744.

(27) Finke, A. D.; Diederich, F. 6,6-Dicyanopentafulvenes: Teaching an Old Dog New Tricks. *Chem. Rec.* **2015**, *15*, 19–30.

(28) Finke, A. D.; Jahn, B. O.; Saithalavi, A.; Dahlstrand, C.; Nauroozi, D.; Haberland, S.; Gisselbrecht, J.-P.; Boudon, C.; Mijangos, E.; Schweizer, W. B.; Ott, S.; Ottosson, H.; Diederich, F. The 6,6-Dycyanopentafulvene Core: A Template for the Design of Electron-Acceptor Compounds. *Chem. - Eur. J.* **2015**, *21*, 8168–8176.

(29) Finke, A. D.; Dumele, O.; Zalibera, M.; Confortin, D.; Cias, P.; Jayamurugan, G.; Gisselbrecht, J. P.; Boudon, C.; Schweizer, W. B.; Gescheidt, G.; Diederich, F. 6,6-Dicyanopentafulvenes: Electronic structure and Regioselectivity in [2 + 2] Cycloaddition-Retroelectrocyclization Reactions. J. Am. Chem. Soc. **2012**, 134, 18139–18146.

(30) Jayamurugan, G.; Gisselbrecht, J.-P.; Boudon, C.; Schoenebeck, F.; Schweizer, W. B.; Bernet, B.; Diederich, F. Expanding the Chemical Space for Push-Pull Chromophores by Non-concerted [2 + 2] and [4 + 2] cycloadditions: Access to a Highly Functionalized 6,6-Dicyanopentafulvene with an Intense, Low-Energy Charge-Transfer Band. *Chem. Commun.* **2011**, *47*, 4520–4522.

(31) Andrew, T. L.; Cox, J. R.; Swager, T. M. Synthesis, Reactivity, and Electronic Properties of 6,6-Dicyanofulvenes. *Org. Lett.* **2010**, *12*, 5302–5305.

(32) King, R. B.; Saran, M. S. Cyclization of Dicyanovinylidene with two Diphenylacetylene Units to Form a 6,6-Dicyanofulvene derivative. *J. Chem. Soc., Chem. Commun.* **1974**, 851–852. (33) Anthony, J. E.; Facchetti, A.; Heeney, M.; Marder, S. R.; Zhan, X. n-Type Organic Semiconductors in Organic Electronics. *Adv. Mater.* **2010**, *22*, 3876–3892.

(34) Brunetti, F. G.; Gong, X.; Tong, M.; Heeger, A. J.; Wudl, F. Strain and Hückel Aromaticity: Driving Forces for a Promising New Generation of Electron Acceptors in Organic Electronics. *Angew. Chem., Int. Ed.* **2010**, *49*, 532–536.

(35) All electrochemical potentials listed in the following have been adjusted to this standard. Electron affinities are based on a HOMO level for ferrocene of -5.1 eV. See ref 36 and literature cited therein for details.

(36) Cardona, C. M.; Li, W.; Kaifer, A. E.; Stockdale, D.; Bazan, G. C. Electrochemical Considerations for Determining Absolute Frontier Orbital Energy Levels of Conjugated Polymers for Solar Cell Applications. *Adv. Mater.* **2011**, *23*, 2367–2371.

(37) Han, Q.; Su, Q.; Tang, L.; Feng, J.; Lu, P.; Wang, Y. Electron Transfer and Aggregate Formation Coinduced Emission Enhancement of 9-Cycloheptatrienylidene Fluorenes in the Presence of Cupric Chloride. J. Phys. Chem. C 2010, 114, 18702–18711.

(38) Wang, Z.; Xing, Y.; Shao, H.; Lu, P.; Weber, W. P. Synthesis and Characterization of 9-(Cycloheptatrienylidene)fluorene Derivatives: Acid-Triggered "Switch on" of Fluorophores. *Org. Lett.* **2005**, *7*, 87–90.

(39) Luisa, M.; Franco, T. M. B.; Celina, M.; Lazana, R. L. R. EPR, ENDOR and TRIPLE Resonance Characterization of Three Paramagnetic Redox Stages of 5-Methylene-5*H*-dibenzo[*a*,*d*]cycloheptene. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 3273–3280.

(40) Daub, J.; Pirzer, E.; Trieschmann, C.; Merz, A. Heptafulvene und Heptafulvenradikalkationen: Ringverengung durch Abspaltung eines C<sub>1</sub>-Fragments bei der Einelektronen-Oxidation von Bis-(dimethylamino)dibenzoheptafulven. *Z. Naturforsch. B* **1984**, *39*, 1586–1592.

(41) Komatsu, K.; Moriyama, T.; Nishiyama, T.; Okamoto, K. Synthesis and Properties of Tetraphenyltriafulvene. *Tetrahedron* **1981**, 37, 721–729.

(42) Yoshida, Z. Novel  $\pi$ -Systems Possessing Cyclopropenylidene Moiety. Pure Appl. Chem. **1982**, 54, 1059–1074.

(43) Yoshida, Z.; Konishi, H.; Sawada, S.; Ogoshi, H. Synthesis and Characterization of the Tetra-aminotriafulvalene Dication. *J. Chem. Soc., Chem. Commun.* **1977**, 850–851.

(44) Dahlstrand, C.; Jahn, B. O.; Grigoriev, A.; Villaume, S.; Ahuja, R.; Ottosson, H. Polyfulvenes: Polymers with Handles That Enable Extensive Electronic Structure Tuning. *J. Phys. Chem. C* **2015**, *119*, 25726–25737.

(45) Schwartz, E.; Koepf, M.; Kitto, H. J.; Nolte, R. J. M.; Rowan, A. E. Helical Polyisocyanides: Past, Present and Future. *Polym. Chem.* **2011**, *2*, 33–47.

(46) Nagata, Y.; Suginome, M. Polyisocyanides, Poly(quinoxaline-2,3-diyl)s, and Related Helical Polymers Used as Chiral Polymer Catalysts in Asymmetric Synthesis. *Polymeric Chiral Catalyst Design and Chiral Polymer Synthesis*, Itsuno, S., Ed.; John Wiley and Sons: Hoboken, NJ, 2011; p 223.

(47) Nolte, R. J. M. Helical Polyisocyanides. *Chem. Soc. Rev.* **1994**, 23, 11–19.

(48) Millich, F. Polymerization of Isocyanides. *Chem. Rev.* **1972**, *72*, 101–113.

(49) Xue, Y.-X.; Chen, J.-L.; Jiang, Z.-Q.; Yu, Z.; Liu, N.; Yin, J.; Zhu, Y.-Y.; Wu, Z.-Q. Living Polymerization of Arylisocyanide Initiated by the Phenylethynyl Palladium(II) Complex. *Polym. Chem.* **2014**, *5*, 6435–6438.

(50) Yamada, T.; Suginome, M. Synthesis of Helical Rod-Coil Multiblock Copolymers by Living Block Copolymerization of Isocyanide and 1,2-Diisocyanobenzene Using Arylnickel Initiators. *Macromolecules* **2010**, *43*, 3999–4002.

(51) Onitsuka, K.; Mori, T.; Yamamoto, M.; Takei, F.; Takahashi, S. Helical Sense Selective Polymerization of Bulky Aryl Isocyanide Possessing Chiral Ester or Amide Groups Initiated by Arylrhodium Complexes. *Macromolecules* **2006**, *39*, 7224–7231.

(52) Onitsuka, K.; Yanai, K.; Takei, F.; Joh, T.; Takahashi, S. Reactions of Heterodinuclear  $\mu$ -Ethynediyl Palladium-Platinum Complexes with Isocyanides: Living Polymerization of Aryl Isocyanides. *Organometallics* **1994**, *13*, 3862–3867.

(53) Ono, R. J.; Todd, A. D.; Hu, Z.; Vanden Bout, D. A.; Bielawski, C. W. Synthesis of a Donor-Acceptor Diblock Copolymer via Two Mechanistically Distinct, Sequential Polymerizations Using a Single Catalyst. *Macromol. Rapid Commun.* **2014**, *35*, 204–209.

(54) Wu, Z.-Q.; Radcliffe, J. D.; Ono, R. J.; Chen, Z.; Li, Z.; Bielawski, C. W. Synthesis of Conjugated Diblock Copolymers: Two Mechanistically Distinct, Sequential Living Polymerizations Using a Single Catalyst. *Polym. Chem.* **2012**, *3*, 874–881.

(55) Wu, Z.-Q. Q.; Liu, D.-F. F.; Wang, Y.; Liu, N.; Yin, J.; Zhu, Y.-Y. Y.; Qiu, L.-Z. Z.; Ding, Y.-S. S. One Pot Synthesis of a Poly(3hexylthiophene)-*b*-poly(quinoxaline-2,3-diyl) Rod-Rod Diblock Copolymer and its Tunable Light Emission Properties. *Polym. Chem.* **2013**, *4*, 4588–4595.

(56) Yu, Z.; Liu, N.; Yang, L.; Jiang, Z.; Wu, Z. One-Pot Synthesis, Stimuli Responsiveness, and White-Light Emissions of Sequence-Defined ABC Triblock Copolymers Containing Polythiophene, Polyallene, and Poly(phenylisocyanide). *Macromolecules* **2017**, *50*, 3204–3214.

(57) Wu, Z.-Q.; Ono, R. J.; Chen, Z.; Bielawski, C. W. Synthesis of Poly(3-alkylthiophene)-*block*-poly(arylisocyanide): Two Sequential, Mechanistically Distinct Polymerizations Using a Single Catalyst. *J. Am. Chem. Soc.* **2010**, *132*, 14000–14001.

(58) Su, M.; Liu, N.; Wang, Q.; Wang, H.; Yin, J.; Wu, Z.-Q. Facile Synthesis of Poly(phenyleneethynylene)-*block*-Polyisocyanide Copolymers via Two Mechanistically Distinct, Sequential Living Polymerizations Using a Single Catalyst. *Macromolecules* **2016**, *49*, 110–119.

(59) Liu, N.; Qi, C.-G.; Wang, Y.; Liu, D. F.; Yin, J.; Zhu, Y.-Y.; Wu, Z.-Q. Solvent-Induced White-Light Emission of Amphiphilic Rod-Rod Poly(3-triethylene glycole thiophene)-*block*-poly(phenyl isocya-nide) Copolymer. *Macromolecules* **2013**, *46*, 7753–7758.

(60) Poly(p-(RO<sub>2</sub>C-)-Ph-NC):  $\lambda_{onset} \approx 480$  nm and  $E_g^{opt} \approx 2.6$  eV: Miyabe, T.; Iida, H.; Banno, M.; Yamaguchi, T.; Yashima, E. Synthesis and Visualization of a Core Cross-Linked Star Polymer Carrying Optically Active Rigid-Rod Helical Polyisocyanide Arms and Its Chiral Recognition Ability. *Macromolecules* **2011**, *44*, 8687–8692.

(61) Poly(R-NC), R = alkyl:  $\lambda_{onset} \approx 340$  nm and  $E_g^{opt} \approx 3.6$  eV: Hu, G.; Li, W.; Hu, Y.; Xu, A.; Yan, J.; Liu, L.; Zhang, X.; Liu, K.; Zhang, A. Water-Soluble Chiral Polyisocyanides Showing Thermoresponsive Behavior. *Macromolecules* **2013**, *46*, 1124–1132.

(62) Pauly, A. C.; Varnado, C. D., Jr.; Bielawski, C. W.; Theato, P. Electrochromic Polyacetylenes with Switchable Visible/Near-IR Absorption Characteristics. *Macromol. Rapid Commun.* **2014**, *35*, 210–213.

(63) Liu, J.; Lam, J. W. Y.; Tang, B. Z. Acetylenic Polymers: Syntheses, Structures, and Functions. *Chem. Rev.* **2009**, *109*, 5799–5867.

(64) Masuda, T. Substituted Polyacetylenes. J. Polym. Sci., Part A: Polym. Chem. 2007, 45, 165–180.

(65) Lam, J. W. Y.; Tang, B. Z. Functional Polyacetylenes. Acc. Chem. Res. 2005, 38, 745-754.

(66) Janoschka, T.; Hager, M. D.; Schubert, U. S. Powering up the Future: Radical Polymers for Battery Applications. *Adv. Mater.* **2012**, *24*, 6397–6409.

(67) Liang, Y.; Tao, Z.; Chen, J. Organic Electrode Materials for Rechargeable Lithium Batteries. *Adv. Energy Mater.* **2012**, *2*, 742–769. (68) Cai, G.; Wang, J.; Lee, P. S. Next-Generation Multifunctional

(68) Cai, G.; Wang, J.; Lee, F. S. Next-Generation Multifunctional Electrochromic Devices. Acc. Chem. Res. **2016**, 49, 1469–1476.

(69) Mortimer, R. J. Electrochromic Materials. *Annu. Rev. Mater. Res.* **2011**, *41*, 241–268.

(70) Gaupp, C. L.; Welsh, D. M.; Rauh, R. D.; Reynolds, J. R. Composite Coloration Efficiency Measurements of Electrochromic Polymers Based on 3,4-Alkylenedioxythiophenes. *Chem. Mater.* **2002**, *14*, 3964–3970.

(71) Sonmez, G. Polymeric Electrochromics. Chem. Commun. 2005, 5251–5259.

(72) Mortimer, J. R. Electrochromic Materials. Chem. Soc. Rev. 1997, 26, 147–156.

(73) Hida, N.; Takei, F.; Onitsuka, K.; Shiga, K.; Asaoka, S.; Iyoda, T.; Takahashi, S. Helical, Chiral Polyisocyanides Bearing Ferrocenyl Groups as Pendants: Synthesis and Properties. *Angew. Chem., Int. Ed.* **2003**, *42*, 4349–4352.

(74) Gomar-Nadal, E.; Mugica, L.; Vidal-Gancedo, J.; Casado, J.; Navarrete, J. T. L.; Veciana, J.; Rovira, C.; Amabilino, D. B. Synthesis and Doping of a Multifunctional Tetrathiafulvalene-Substituted Polyisocyanide. *Macromolecules* **2007**, *40*, 7521–7531.

(75) Gomar-Nadal, E.; Veciana, J.; Rovira, C.; Amabilino, D. B. Chiral Teleinduction in the Formation of a Macromolecular Multistate Chiroptical Redox Switch. *Adv. Mater.* **2005**, *17*, 2095–2098.

(76) Ugi, I.; Lohberger, S.; Karl, R. The Passerini and Ugi Reactions. *Comp. Org. Synth.* **1991**, *2*, 1083–1109.

(77) Ugi, I.; Werner, B.; Dömling, A. The Chemistry of Isocyanides, their Multicomponent Reactions and their Libraries. *Molecules* **2003**, *8*, 53–66.

(78) Lang, S. Unravelling the Labyrinth of Palladium-Catalysed Reactions Involving Isocyanides. *Chem. Soc. Rev.* **2013**, *42*, 4867–4880.

(79) Qiu, G.; Ding, Q.; Wu, J. Recent Advances in Isocyanide Insertion Chemistry. *Chem. Soc. Rev.* **2013**, 42, 5257–5269.

(80) Harvey, P. D. Chemistry, Properties and Applications of the Assembling 1,8-Diisocyano-*p*-menthane, 2,5-Dimethyl-2',5'-diisocyanohexane and 1,3-Diisocyanopropane 91 Ligands and their Coordination Polynuclear Complexes. *Coord. Chem. Rev.* 2001, 219–221, 17–52.

(81) Singleton, E.; Oosthuizen, H. E. Metal Isocyanide Complexes. *Adv. Organomet. Chem.* **1983**, *22*, 209–310.

(82) Yamamoto, Y. Zerovalent Transition Metal Complexes of Organic Isocyanides. *Coord. Chem. Rev.* **1980**, 32, 193–233.

(83) Treichel, P. M. Transition Metal-isocyanide Complexes. Adv. Organomet. Chem. 1973, 11, 21–86.

(84) Xu, Y.; Hu, X.; Shao, J.; Yang, G.; Wu, Y.; Zhang, Z. Hydration of Alkynes at Room Temperature Catalyzed by Gold(I) Isocyanide Compounds. *Green Chem.* **2015**, *17*, 532–537.

(85) Vicenzi, D.; Sgarbossa, P.; Biffis, A.; Tubaro, C.; Basato, M.; Michelin, R. A.; Lanza, A.; Nestola, F.; Bogialli, S.; Pastore, P.; Venzo, A. Venzo A. Platinum(II) Complexes with Novel Diisocyanide Ligands: Catalysts in Alkyne Hydroarylation. *Organometallics* **2013**, 32, 7153–7162.

(86) Luo, C.; Yang, H.; Mao, R.; Lu, C.; Cheng, G. An Efficient Au(I) Catalyst for Double Hydroarylation of Alkynes with Heteroarenes. *New J. Chem.* **2015**, *39*, 3417–3423.

(87) Bueldt, L. A.; Wenger, O. S. Chromium(0), Molybdenum(0), and Tungsten(0) Isocyanide Complexes as Luminophores and Photosensitizers with Long-Lived Excited States. *Angew. Chem., Int. Ed.* **2017**, *56*, 5676–5682.

(88) Malzkuhn, S.; Wenger, O. S. Luminescent Ni(0) complexes. Coord. Chem. Rev. 2018, 359, 52–56.

(89) Bueldt, L. A.; Wenger, O. S. Luminescent Complexes Made from Chelating Isocyanide Ligands and Earth-Abundant Metals. *Dalton Transactions* **2017**, *46*, 15175–15177.

(90) Guo, X.; Wenger, O. S. Reductive Amination by Photoredox Catalysis and Polarity-Matched Hydrogen Atom Transfer. *Angew. Chem., Int. Ed.* **2018**, *57*, 2469–2473.

(91) Larsen, C. B.; Wenger, O. S. Photophysics and Photoredox Catalysis of a Homoleptic Rhenium(I) Tris(diisocyanide) Complex. *Inorg. Chem.* **2018**, *57*, 2965–2968.

(92) Bueldt, L. A.; Larsen, C. B.; Wenger, O. S. Luminescent Ni<sup>0</sup> Diisocyanide Chelates as Analogues of Cu<sup>I</sup> Diimine Complexes. *Chem. - Eur. J.* **2017**, *23*, 8577–8580.

(93) Bueldt, L. A.; Guo, X.; Vogel, R.; Prescimone, A.; Wenger, O. S. A Tris(diisocyanide)chromium(0) Complex Is a Luminescent Analog of Fe(2,2'-Bipyridine)<sub>3</sub>. *J. Am. Chem. Soc.* **2017**, *139*, 985–992.

(94) Bueldt, L. A.; Guo, X.; Prescimone, A.; Wenger, O. S. A Molybdenum(0) Isocyanide Analogue of Ru(2,2'-Bipyridine)32+: A Strong Reductant for Photoredox Catalysis. *Angew. Chem., Int. Ed.* **2016**, 55, 11247–11250.

(95) Knorn, M.; Rawner, T.; Czerwieniec, R.; Reiser, O. [Copper-(phenanthroline)(Bisisonitrile)]<sup>+</sup>-Complexes for the Visible-Light-Mediated Atom Transfer Radical Addition and Allylation Reactions. *ACS Catal.* **2015**, *5*, 5186–5193.

(96) Fujisawa, K.; Okuda, Y.; Izumi, Y.; Nagamatsu, A.; Rokusha, Y.; Sadaike, Y.; Tsutsumi, O. Reversible Thermal-mode Control of Luminescence from Liquid-crystalline Gold(I) Complexes. *J. Mater. Chem. C* 2014, 2, 3549–3555.

(97) Hagedorn, I.; Etling, H. Darstellung von  $\alpha,\beta$ -Ungesättigtenund  $\beta$ -Keto-isonitrilen. Angew. Chem. **1961**, 73, 26–27.

(98) Spallarossa, M.; Wang, Q.; Riva, R.; Zhu, J. Synthesis of Vinyl Isocyanides and Development of a Convertible Isonitrile. *Org. Lett.* **2016**, *18*, 1622–1625.

(99) Barton, D. H. R.; Bowles, T.; Husinec, S.; Forbes, J. E.; Llobera, A.; Porter, E. A.; Zard, S. Reductive Formylation of Oximes; An Approach to The Synthesis of Vinyl Isocyanides. *Tetrahedron Lett.* **1988**, *29*, 3343–3346.

(100) Evans, J. R.; Napier, E. F.; Yates, P. Isolation of a New Antibiotic from a Species of Pseudomonas. *J. Antibiot.* **1976**, *29*, 850–852.

(101) Li, S.; Lowell, A. N.; Yu, F.; Raveh, A.; Newmister, S. A.; Bair, N.; Schaub, J. M.; Williams, R. M.; Sherman, D. H. Hapalindole/ Ambiguine Biogenesis is Mediated by a Cope Rearrangement, C-C Bond-Forming Cascade. J. Am. Chem. Soc. 2015, 137, 15366–15369. (102) Yamaguchi, T.; Miyake, X.; Miyamura, A.; Ishiwata, N.;

Tatsuta, K. Structure-activity Relationships of Xanthocillin Derivatives as Thrombopoietin Receptor Agonist. J. Antibiot. 2006, 59, 729–734.

(103) Sakai, R.; Nakamura, T.; Nishino, T.; Yamamoto, M.; Miyamura, A.; Miyamoto, H.; Ishiwata, N.; Komatsu, N.; Kamiya, H.; Tsuruzoe, N. Xanthocillins as Thrombopoietin Mimetic Small Molecules. *Bioorg. Med. Chem.* **2005**, *13*, 6388–6393.

(104) Hagedorn, I.; Eholzer, U.; Lüttringhaus, A. Beiträge zur Konstitutionsermittlung des Antibiotikums Xanthocillin. *Chem. Ber.* **1960**, *93*, 1584–1590.

(105) Jakobsen, P. N-Isocyanoimines. Preparation and Characterization. *Scand. Chim. Acta B* **1976**, *30*, 995–996.

(106) Hagedorn, I. Neuartige Isonitrile. Angew. Chem. 1963, 75, 305-305.

(107) Reggelin, M.; Scholz, J.; Hamburger, M. Helically Chiral Poly(quinoxalin-2,3-diyl)s: Toward the Synthesis of Stereoregular Polymeric Organocatalysts. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, 47, 4830–4839.

(108) Ito, Y.; Ihara, E.; Murakami, M. Enantioselective Polymerization of 1,2-Dicyanoarenes - Syntheses of Optically Active, Helical Poly(quinoxaline-2,3-diyl)s. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1509–1510.

(109) Electron-rich trialkylphosphines are 7–9 orders of magnitude more basic than triarylphosphines:  $pK_a([Ph_3P-H]^+) = 2.73$ ,  $pK_a((tBu_3P-H]^+) = 11.40$ ,  $pK_a([cHx_3P-H]^+) = 9.65$ , adopted from: Allman, T.; Goel, R. G. The Basicity of Phosphines. *Can. J. Chem.* **1982**, 60, 716–722. In Wittig-type coupling reactions this presumably translates into a significantly lower C–H acidity of  $\alpha$ -protons and hence into a higher reactivity and nucleophilicity of the corresponding ylids/ylenes.

(110) Ogliaruso, M. A.; Romanelli, M. G.; Becker, E. I. Chemistry of Cyclopentadienones. *Chem. Rev.* **1965**, *65*, 261–367.

(111) Díaz, J. E.; Gruber, N.; Orelli, L. R. 1,n-Diamines. Part 4: Synthesis of 1-Aryl-2-alkyl-1,4,5,6,7,8-hexahydro-1,3-diazocines. *Tetrahedron Lett.* **2011**, *52*, 6443–6445.

(112) Au(CNPh)Cl:  $\tilde{\nu} = 2230 \text{ cm}^{-1}$ ; Au(CNPh)C<sub>6</sub>F<sub>5</sub>:  $\tilde{\nu} = 2212 \text{ cm}^{-1}$ . Usón, R.; Laguna, A.; Vicente, J.; García, J.; Bergareche, B.; Brun, P. Neutral Isocyanide and Carbene Pentafluorophenyl Complexes of Gold(I) and Gold(III). *Inorg. Chim. Acta* **1978**, *28*, 237–243.

(113) Au(CN-C<sub>6</sub>H<sub>4</sub>-R)Cl:  $\tilde{\nu} = 2222 \text{ cm}^{-1}/2223 \text{ cm}^{-1}$ . Zhang, Y.; Maverick, A. W. Preparation of an Isocyano- $\beta$ -diketone via its Metal Complexes, by Use of Metal Ions as Protecting Groups. *Inorg. Chem.* **2009**, 48, 10512–10518.

(114) Hammet parameters (meta/para,  $\sigma_m/\sigma_p$ ): -NC:  $\sigma_m = 0.48$ and  $\sigma_p = 0.49$ ; -NO<sub>2</sub>:  $\sigma_m = 0.71$  and  $\sigma_p = 0.78$ ; -CH=N-Ph:  $\sigma_m = 0.35$  and  $\sigma_p = 0$ ; NH-CHO:  $\sigma_m = 0.19$  and  $\sigma_p = 0.00$ ; -NH<sub>2</sub>:  $\sigma_m = -0.16$  and  $\sigma_p = -0.66$ ; -COMe:  $\sigma_m = 0.38$  and  $\sigma_p = 0.50$ . Figures adopted from ref 115.

(115) Hansch, C.; Leo, A.; Taft, R. W. A Survey of Hammett Substituent Constants and Resonance and Field Parameters. *Chem. Rev.* **1991**, *91*, 165–195.

(116) Jung, H.; Shaikh, A. U.; Heflich, R. H.; Fu, P. P.; Hartman, P. E. Nitro Group Orientation, Reduction Potential, and Direct-acting Mutagenicity of Nitro-Polycyclic Aromatic Hydrocarbons. *Environ. Mol. Mutagen.* **1991**, *17*, 169–180.

(117) Banide, E. V.; O'Connor, C.; Fortune, N.; Ortin, Y.; Milosevic, S.; Müller-Bunz, H.; McGlinchey, M. J. Syntheses, X-ray Crystal Structures and Reactivity of Fluorenylidene- and Dibenzosuberenylidene-allenes: Convenient Precursors to Dispirotetracenes, Diindenotetracenes and 2-Phenyl-11bH-dibenz[cd,h]azulene. Org. Biomol. Chem. 2010, 8, 3997–4010.

(118) Castiglione, F.; Ganazzoli, F.; Malpezzi, L.; Mele, A.; Panzeri, W.; Raffaini, G. Inclusion Complexes of  $\beta$ -Cyclodextrin with Tricyclic Drugs: an X-ray Diffraction, NMR and Molecular Dynamics Study. *Beilstein J. Org. Chem.* **2017**, *13*, 714–719.

(119) Zeng, R.-H. 5-(4-Bromobenzylindene]-5*H*-dibenzo[*a*,*d*][7]annulene. Acta Crystallogr. **2008**, E63, o589.

(120) Dbs =  $CH-CH=C_5H_4$ : Lindner, H. J.; Hafner, K.; Romer, M.; von Gross, B. Cyclisch Konjugierte 5- und 7-Ringsysteme, III. Synthese und Struktur des  $\alpha$ -(6-Fulvenyl)dibenzo[*a*,*e*]heptafulvenes. Liebigs Ann. 1975, 1975, 731–742.

(121) Pammer, F.; Jäger, J.; Rudolf, B.; Sun, Y. Soluble Head-to-Tail Regioregular Polythiazoles: Preparation, Properties and Evidence for Chain-Growth Behavior in the Synthesis via Kumada-Coupling Polycondensation. *Macromolecules* **2014**, *47*, 5904–5912.

(122) (a)  $\tilde{\nu} = 1670 \text{ cm}^{-1}$ : Kamer, P. C. J.; Nolte, R. J. M.; Drenth, W. Screw Sense Selective Polymerization of Achiral Isocyanides Catalyzed by Optically Active Nickel(II) Complexes. *J. Am. Chem. Soc.* **1988**, *110*, 6818–6825.

(123)  $\tilde{\nu} = 1616$ , 1593 cm<sup>-1</sup>: Yamamoto, Y.; Yamazaki, H. The Oligomerization and Co-oligomerization of Active Methylene Compounds and Isocyanides Catalyzed by Octaisocyanidedicobalt. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 787–789.

(124) 1625 cm<sup>-1</sup>: Sawai, H.; Takizawa, T. Reaction of Isocyanide with Mercuric Chloride. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1906–1908.

(125) Amabilino, D. B.; Ramos, E.; Serrano, J. L.; Sierra, T.; Veciana, J. Chiral Teleinduction in the Polymerization of Isocyanides. *Polymer* **2005**, *46*, 1507–1521.

(126) Lou, X.; Li, B.; de Waal, B. F. M.; Schill, J.; Baker, M. B.; Bovee, R. A. A.; van Dongen, J. L. J.; Milroy, L.-G.; Meijer, E. W. Fragmentation of Organic Ions Bearing Fixed Multiple Charges Observed in MALDI MS. J. Mass Spectrom. **2018**, *53*, 39–47.

(127) Tang, W.; Zhu, L.; Smith, L. M. Controlling DNA Fragmentation in MALDI-MS by Chemical Modification. *Anal. Chem.* **1997**, *69*, 302–312.

(128) Kamer, P. C. J.; Cleij, M. C.; Nolte, R. J. M.; Harada, T.; Hezemans, A. M. F.; Drenth, W. Atropisomerism in Polymers. Screwsense Selective Polymerization of Isocyanides by Inhibiting the Growth of one Enantiomer of a Racemic Pair of Helices. *J. Am. Chem. Soc.* **1988**, *110*, 1581–1586.

(129) Clericuzio, M.; Alagona, G.; Ghio, C.; Salvadori, P. Theoretical Investigations on the Structure of Poly(iminomethylenes) with Aliphatic Side Chains. Conformational Studies and Comparison with Experimental Spectroscopic Data. *J. Am. Chem. Soc.* **1997**, *119*, 1059–1071.

(130) The absorption onsets seemingly differ from those measured for drop-cast films. This is largely owed to experimental artifacts originating from dispersion and absorption of the experimental setup and is evident from the nonzero baseline at wavelength > 600 nm. Further baseline correction was not possible without severe distortion of the spectra.