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Photoactive boron-nitrogen-carbon hybrids: from azo-borazines to polymeric materials

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ABSTRACT: In this paper, we describe the synthetic routes for preparing a novel switchable BNC-based chromophore, composed of a borazine core peripherally functionalized with azobenzene moieties. Capitalizing on the Pd-catalyzed Suzuki cross-coupling reaction between a tris-triflate borazine and an organoboron azobenzene derivative, a photoswitchable azo-borazine derivative was successfully prepared. The molecule showed reversible E/Z photoisomerization upon irradiation at the maximum of the intense π-π* absorption feature (360 nm). X-Ray crystallographic investigations revealed a non-planar orientation of the three azobenzene moieties and the trans configuration of the -N=N- bonds. Building on the synthetic versatility of the borazine-azobenzene derivative, we used this photoactive scaffold to engineer soluble BN-doped polythiophene polymers. Photophysical characterization performed in solvents of different polarity, suggested that the polymer undergoes intramolecular charge-transfer (ICT).
INTRODUCTION

Stimuli-responsive molecules and materials capable of undergoing reversible structural changes are of great interest for future technology.\(^1\) A typical example is the E/Z photoisomerization of azobenzenes, which is characterized by an irradiation-induced Z→E isomerization between the thermodynamically favored, stretched E-isomer and its Z-isomer. The photoisomerization is accompanied by a dramatic change in electronic structure, geometric shape, and polarity, resulting into the spatiotemporal control of the conformational and overall structural properties of molecular systems.\(^2\) Notable applications include their integration into architectures expressing functional properties in materials science,\(^3\) biology\(^4\) and molecular recognition.\(^1c, 5\)

The replacement of C=C units by more polarized BN couples is a versatile functionalization strategy to tailor the optoelectronic characteristics of organic π-systems without significant structural alteration of the nanostructure.\(^6\) The BN/CC isosterism concept goes back to the seminal discovery of the borazine (H\(_3\)B\(_3\)N\(_3\)H\(_3\)) by Stock and Pohlant in 1926.\(^7\) The borazine core is commonly referred to as the “inorganic benzene”, owing to its iso-electronic and iso-structural relationships with benzene.\(^7\) Accordingly, borazine and its derivatives are valuable scaffolds to be inserted as doping units in graphitic-based carbon materials to tailor their optoelectronic characteristics\(^8\) and self-assembly properties on surfaces.\(^9, 23\) Important examples include dendritic borazine-doped polyphenylenes,\(^10\) borazine-doped coronenes\(^11\) and borazino-based polymers.\(^10, 12\) Not only borazine-based materials, but also hybrid BNC-based architectures are attracting increasing consideration due to their thermal stability, mechanical robustness and tunable optoelectronic properties.\(^13\) In this respect, the incorporation of BN units into π-conjugated polymers is emerging as an evident route to broaden the scope of organic electronic materials.\(^6d, 13b, 14\) For their part, π-conjugated polymers have revolutionized the field of optoelectronics\(^15\) and are nowadays used to produce low-cost, large-area, and flexible electronic devices.\(^16\) In these materials, the tailoring of the LUMO/HOMO energy levels for a given application is of high importance.\(^15d, 17\) Among the different strategies, the incorporation of heteroatomic units into the polymer structures such as boron and nitrogen atoms revealed to be a powerful strategy to prepare isostructural molecular\(^6c, 11, 18\) and polymeric materials\(^6d, 14a, 19\) bearing strong local dipole moments.\(^14a, 14b, 20\)

Owing to the possibility of functionalizing the borazine core with different groups on the aryl substituents at the N and B atoms,\(^6c, 7d, 21\) and to the easy polymerization of thiophenes for producing low-cost and flexible electronic devices, we have envisaged to employ the borazine (B\(_3\)N\(_3\)) as the core skeleton and azobenzene as photo-responsive unit to engineer new photoswitchable molecular BNC hybrid materials (Fig. 1). Considering the conductive properties of poly(3-hexylthiophene) (P3HT),\(^22\) the 3-hexylthiophene scaffold was selected as monomeric unit to develop the polymer material. Also, we were not unmindful to exploit the side alkyl chains to enhance the solubility of the final material (Fig. 1b).
RESULTS AND DISCUSSION

Synthesis the azo-borazine core. Three classes of derivatives were targeted as photoactive BNC molecular scaffold: azo-borazine-1, azo-borazine-2, and azo-borazine-3 (Fig. 1a). Due to the chemical sensitivity of the B_3N_3 core under the reaction conditions to form azobenzene moiety, azo-borazine-1 and azo-borazine-2 could not be prepared (see SI for the attempts). Thus, we decided to follow a convergent synthetic pathway, in which a precursor B_3N_3 core is reacted with azobenzene moieties, avoiding the need to use strong oxidizing conditions to form the azo-functional group. It is following this approach, that we prepared azo-borazine-3 reacting a suitable aryl halide or related electrophile (i.e., ArOTf) with an organoboron derivative of a given azobenzene under the Suzuki cross-coupling reaction conditions (Scheme 1). Specifically, the tert-butylidemethylsilyl (TBDMS)-protected borazine derivative 3 was prepared following a modified protocol^{8, 23} of that reported by Groszos and Stafiej^{24} and later by Yamaguchi.^21^ The synthesis started with the reaction of aniline 1 with BCl_3 under refluxing conditions gave intermediate tri-B-chloro-tri-N-phenylborazine that, upon reaction with TBDMS-protected ArLi, could be transformed into TBDMS-protected borazine derivative 3 in 49% yield (reaction a-b). Removal of the TBDMS protecting group with TBAF and successive esterification with Tf_2O in pyridine, led to key intermediate tris-triflate borazine 4 in 75% yield (reactions c-d).^{10} White suitable crystals were obtained from evaporation of a solution containing either compound 3 (Fig. 2a) or compound 4 (Fig. 2b) in CHCl_3 belonging to the P-1 and P2_1/n space groups, respectively. As expected, the X-ray molecular structures show the quasi-orthogonal arrangement of the aryl moieties, which place the methyl substituents atop the B atoms, sterically shielding the electrophilic B-centers.^25^ In parallel, the synthesis of the organoboron derivative of
azobenzene 8 was performed through the Mills reaction, starting from commercially available nitrosobenzene 5 and 4-iodoaniline 6 followed by Miyaura borylation reaction (Scheme 1, reactions e-f). Final Suzuki cross-coupling reaction between borazine 4 and azobenzene-boronic ester 8 yielded desired azo-borazine-3 in 83% yield (Scheme 1, reaction g).

Scheme 1. Synthetic approach toward the preparation of azobenzene-borazine-based BNC hybrid materials. Reagents and conditions: (a) BCl₃, toluene, reflux, 18 h; (b) 2, tert-BuLi, THF, -84 °C to r.t., 16 h, 49%; (c) TBAF, THF, 0 °C, 2 h; (d) Tf₂O, pyridine, r.t., 16 h, 75%; (e) AcOH, r.t., 18 h, 81%; (f) B₂Pin₂, KOAc, [Pd(dpff)Cl₂CH₂Cl₂], DMF, 80%; (g) K₂CO₃, [Pd(PPh₃)₄], 1,4-dioxane:H₂O (3:1 v/v), 105 °C, 18 h, 83%. TBAF: tetra-butylammonium fluoride. Tf₂O: tri-fluoromethanesulfonic anhydride. B₂Pin₂: 4,4',5,5'-Octamethyl-2,2'-bi-1,3,2-dioxaborolane. [Pd(dpff)Cl₂CH₂Cl₂]: [1,1’-bis(diphenylphosphino)ferrocene dichloropalladium(II)] dichloromethane adduct.

Figure 2. X-ray determined molecular structure of a) compound 3 and b) compound 4 (Atom colors: blue N, pink B, red O, yellow Si, orange S, light green F, gray C; hydrogen atoms are omitted for clarity). Space group: a) P-1 b) P2₁/n.
**Azo-borazine-3** derivative was characterized using NMR, IR, and MALDI-ToF spectrometry. At first, **azo-borazine-3** was identified by MALDI-ToF through the detection of the peak corresponding to the molecular ion at m/z 1162.6010 ([M+H]+) (caled for C_{78}H_{67}B_{3}N_{9}+ 1162.5793). \(^1\)H NMR analysis further confirmed the chemical structure (Fig. 3) and the \(^{11}\)B NMR spectrum showed a broad peak at 36.0 ppm (inset Fig. 3), consistent with a boron atom substituted by two N-atoms and linked to one carbon atom. Finally, IR spectrum revealed an intense band at 1353 cm\(^{-1}\), characteristic of the B-N stretching in a borazine core.\(^8\)

**Figure 3.** \(^1\)H NMR spectrum of **azo-borazine-3** (CD\(_2\)Cl\(_2\), 400 MHz, 25 °C). Inset: a zoom of the region 6.60-8.00 ppm and \(^{11}\)B NMR spectrum (CDCl\(_3\), 128 MHz, 25 °C).

Small needle-like orange crystals of **azo-borazine-3** suitable for X-ray diffraction were grown by vapor diffusion of hexane to a solution of **azo-borazine-3** in CH\(_2\)Cl\(_2\). Similarly to borazine 4, the X-ray molecular structure shows the quasi-orthogonal arrangement of the aryl moieties. The X-ray analysis confirms the trans configuration of the \(-\text{N=N-}\) functional groups and reveals the non-planar arrangement of the three aryl rings at the solid state (Fig. 4a). A deviation from orthogonal arrangement of the aryl substituents and the borazine ring is clearly observed with inter-planar angles of 122.6° between the borazine ring and phenyl groups, and of 108.9° between both phenyl and xylyl groups. As previously observed in the literature,\(^8\),\(^25\) the intra-annular distance values between boron and nitrogen atoms are between 1.43 and 1.46 Å, with the internal angle of the borazine cycle between 122.7° and 117.03° (BNB and NBN, respectively).
Figure 4. (a) Frontal (top) and side (bottom) views of the X-ray crystal structure of azo-borazine-3 (with the B-N distances in Å), (b) packing diagram viewed along the a axis and (c) Crystal packing, along the a crystallographic direction, showing zigzag stacking shape of the molecules. (Atom colors: blue N, pink B, gray C; hydrogen atoms are omitted for clarity). Space group: P21/c.
Notably, the azobenzene moieties in the crystal exist in a twisted shape with respect to the B-Aryl groups (Fig. 4a). Interestingly, the crystal packing four azo-borazine-3 molecules stack in parallelepiped-like fashion. The borazine cores constituting the four faces of the arrangement, with each B-center facing the N-center forming layers separated by a distance of 6.99 and 19.93 Å (Fig. 4b). Each layer is formed by borazine molecules lying side by side on the same plane and separated by a distance of 20.22 Å (Fig. 4c) and the adjacent layers are assembled in a zigzag-like stacking forming a 3D porous assembly (Fig. 4d).

Photo- and thermal-isomerizations of the azo-borazine-3. The photo-isomerization reaction between the E- and Z-isomers of azo-borazine-3 was studied in toluene (5·10⁻⁶ M) at r.t. (Fig. 5). The molecule exhibits two UV absorption bands at 360 nm and 450 nm, which are attributed to π-π* (of the E-isomer) and n-π* (of the Z-isomer) electronic transitions, respectively. When irradiated at 360 nm, remarkable changes are observed in the absorption spectra of the azo-borazine-3 (Fig. 5a), with an intense and fast increase of a new band centered at around 290 nm and a substantial increase of the intensity of the n-π* band at 450 nm (inset of Fig. 5a) with a concomitant disappearance of the π-π* absorption band. Neat isosbestic points are maintained throughout the photoirradiation experiments, showing the clean occurrence of the nearly quantitative E→Z isomerization after 3 min of irradiation, while no evolution in the UV-Vis absorption was observed even after 20 min of irradiation at 360 nm. On the other hand, irradiation at 450 nm causes the Z→E isomerization, as observed by the simultaneous decrease and increase of the n-π* and π-π* absorption bands, respectively. The full restoring of the E-isomer was not observed even after 23 min of irradiation at 450 nm (Fig. 5b).

Figure 5. Reversible change in the absorption spectra of a 5·10⁻⁶ M solution of azo-borazine-3 in toluene under irradiation at (a) 360 nm and (b) 450 nm at r.t. (23 °C). Inset: UV absorption at 360 nm of azo-borazine-3 in toluene as a function of irradiation time.

Repetitive photo-induced switching cycles evidenced an excellent fatigue resistance and remarkable photostability of azo-borazine-3 (Fig. 6). As expected, the borazine core has little influence on the photochemical properties, with the azo-borazine-3 showing the typical E/Z switching behavior of standard azobenzenes. The UV absorbing BN-core does not interfere with the excitation properties of the azobenzene moieties. The thermal Z→E isomerization (obtained after irradiation at 360 nm for 3 min) was realized by measuring the absorbance of a 5·10⁻⁶ M solution of azo-borazine-3 in toluene at different temperatures (Fig. 7a). As shown in Figure 7, the
thermal $Z \rightarrow E$ interconversion occurs very slowly, and the spectral profile of the $E$-isomer is fully recovered only upon heating at 100 °C.

![Graph](image)

**Figure 6.** Repetitive photoinduced switching cycles of the azo-borazine-3 obtained by alternating irradiations at 360 and 450 nm (5·10⁻⁶ M solution in toluene at 23 °C).

![Graph](image)

**Figure 7.** UV-Vis measurements of the thermal $Z \rightarrow E$ isomerization of azo-borazine-3 after sample irradiation at 360 nm (5·10⁻⁶ M in toluene) (a) and at r.t. in the dark (b).

**Self-assembly behavior of azo-borazine-3.** To investigate the aggregation properties of azo-borazine-3, a THF/water mixture solvent was used to trigger the self-assembly into nanoparticles. Particles were formed by...
dissolving the azo-borazine-3 in THF containing various fractions \((f_w)\) of water at a concentration of \(4.6 \times 10^{-6} \text{ M}\) under sonication at 40 °C for 15 min. As shown in Figure 8a, in pure THF the absorption spectra of the azo-borazine-3 consist of a strong absorption peak at 360 nm and a very weak band around 450 nm attributed to \(\pi-\pi^*\) and \(n-\pi^*\) electronic transitions of the azobenzene unit, respectively. Upon increasing the water fraction, the absorption spectra broadened and showed a hypochromic effect in intensity, suggesting the formation of aggregates.\(^{28}\) Similarly, emission measurements were recorded for the azo-borazine-3 under excitation at 360 nm (Fig. 8b). Azo-borazine-3 in THF exhibits an emission maximum at 406 nm with a fluorescence quantum yield \((\Phi_f)\) of 0.82%. An appreciable enhancement of the emission intensity was observed with increasing fractions of water, with the maximum being at 406 nm \((\Phi_f = 3.28\%, f_w = 95\%)\). In these compounds, intramolecular rotations play a crucial role to populate the non-radiative decay channels for the excited states and enhance their rates.\(^{29}\) The free intramolecular torsional motion in solution favours the non-radiative decays that are the responsible for the weak emission in THF.\(^{30}\) However, these torsional motions are hindered in the aggregated state. The enhancement of the emission in the aggregated state also suggested a suppression of the concentration quenching in the aggregated state by amplified intermolecular distances resulting from the partially distorted structure of the fluorogenic units.\(^{31}\)

![Figure 8](image.png)

Figure 8. (a) Absorption and (b) fluorescence \((\lambda_{\text{excitation}} = 360 \text{ nm})\) spectra of the azo-borazine-3 in THF with increasing water contents \((f_w \%)\) recorded at r.t. (The final concentration was \(4.6 \times 10^{-6} \text{ M}\)).

Then, we investigated the morphology of the as-formed aggregates using transmission electron microscope (TEM). Spherical aggregates with different diameters from 90 nm to \(~ 600 \text{ nm}\) were obtained for samples containing azo-borazine-3 prepared in a THF/H\(_2\)O mixture \((f_w = 95\%)\) (Fig. 9a-d). Notably, some of the particles stick together to form large aggregates (Fig. 9e). Dynamic light scattering (DLS) measurements (Fig. 9f) performed on the same sample confirmed the presence of aggregates displaying hydrodynamic diameters ranging from 110 ± 20 nm to 295 ± 150 nm, together with larger particles with hydrodynamic diameters of 4 ± 1 µm. Since the formation of the nanoparticles involves stepwise addition of a poor solvophobic solvent (H\(_2\)O) to a stable solution of the azo-borazine-3 in THF, the solubility of the molecule is gradually reduced upon addition of water, leading to the formation of aggregates. Larger nanoparticles are formed either through attractive \(VdW\) or dipolar forces. As previously suggested by Ajayaghosh and co-workers for azobenzene-based nanodots,\(^{38}\) the growth of these aggregates could also be attributed to a light-driven “Ostwald ripening”-type mechanism.\(^{32}\)
Synthesis of the borazine-doped polythiophene-based polymer. For the application of azo-borazine as building block in polymers main chain, the key issue is to introduce reactive groups on repetitive units. Therefore, we synthesized bis-triflate borazine derivative (bis-OTf-borazine) 9 starting from the tris-OTf-borazine 4 and azobenzene-functionalized thiophene derivative \((1E,1'E)-2,2'-(3-hexylthiophene-2,5-diyl)bis(2-octyl-4,1-phenylene)bis(I-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)diazene)\) (AB-3HT-(BPin))\(_2\) 21 as monomers. Bis-OTf-borazine 9 was prepared in 30% yield via Suzuki cross-coupling reaction between tris-OTf-borazine 4 and phenylboronic acid (Scheme 2, reaction a). In parallel, AB-3HT-(BPin)\(_2\) 21 monomer was prepared starting from 1-bromo-2-nitrobenzene 10 and 1-octyne through Sonogashira cross-coupling reaction leading to 1-nitro-2-(oct-1-yn-1-yl)-benzene 11 in 90% yield (Scheme 2, reaction b). Compound 11 was quantitatively reduced using Pd-catalyzed hydrogenation yielding compound 12 (Scheme 2, reaction c). A regio-selective bromination of 12 by pyridinium hydrobromide perbromide gave 4-bromo-2-octylaniline 13 in 71% yield (Scheme 2, reaction d). Miyaura borylation of compound 13 in 1,4-dioxane provided 2-octyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline 14 in 50% yield (Scheme 2, reaction e). Compound 14 was then coupled to 3-hexyl-2,5-diiodothiophene 16, prepared in 90% yield from 3-hexylthiophene 15 (Scheme 2, reaction f), via Suzuki cross-coupling reaction yielding \((4,4'-(3-hexylthiophene-2,5-diyl)bis(2-octyl-4,1-phenylene)bis(I-(4-bromophenyl)diazene)\) AB-3HT-Br\(_2\) 20 in 45% yield (Scheme 2, reaction i). Miyaura borylation of compound 20 led to the desired monomer AB-3HT-(BPin)\(_2\) 21 in 65% yield (Scheme 2, reaction j). Finally, the synthesis of the P(AB-3HT-borazine) polymer was carried out using a standard Suzuki cross-coupling polycondensation reaction (Scheme 2, reaction k). The molecular weight estimated by gel permeation chromatography (GPC) relative to polystyrene standard in THF (+2% Et\(_3\)N) at 30 °C was 13.2 kDa with a dispersity (D\(_M\)) of 1.92 and a degree of polymerization (DP) of 9.
Scheme 2. Synthetic routes for preparing P(AB-3HT-borazine) polymer. Reagents and conditions: (a) Phenylboronic acid, [Pd(PPh₃)₄], K₂CO₃, 1,4-dioxane-water (3:1 v/v), 100 °C, 8 h, 30 %; (b) 1-octyne, [Pd(PPh₃)₄], CuBr, Et₃N, 90 °C, 15 h 90%; (c) H₂ (1 atm), Pd/C (10 wt.%), EtOH, r.t., 6 h, 95%; (d) pyridinium hydrobromide perbromide, THF, r.t., 1 h 45, 71%; (e) B₃Pin₂, [Pd(dppf)Cl₂]:CH₂Cl₂, KOAc, 1,4-dioxane, 90 °C, 24 h, 50%; (f) NIS, AcOH:CHCl₃ (3:1 v/v), r.t., 24 h, 30%; (g) [Pd(PPh₃)₄], K₂CO₃, 1,4-dioxane: H₂O (3:1), 105 °C, 24 h, 30%; (h) oxone, CH₂Cl₂:H₂O (1.3 v/v), r.t., 3 h, quant.; (i) AcOH:EtOAc (1:1 v/v), 40 °C, 36 h, 45%; (j) B₃Pin₂, [Pd(dppf)Cl₂]:CH₂Cl₂, AcOK, 1,4-dioxane, 90 °C, 24 h, 65%; (k) [Pd(PPh₃)₄], K₂CO₃, toluene:water (2:0.2 v/v), 100 °C, 48 h, 60%. NIS: N-iodosuccinimide.

The polymer is soluble in common organic solvents such as CH₂Cl₂, chloroform, THF, toluene and insoluble in acetone, methanol and n-heptane. ¹H NMR spectrum of P(AB-3HT-borazine) polymer in CDCl₃ (Fig. 10) showed all characteristic peaks of its repeating units. The low-field shifting of the aromatic proton resonance of the (OTf)-aryl group of the borazine unit from 6.49 ppm in the starting material (bis-OTf-borazine) to 6.92 ppm in the polymer structure, suggests that the desired polymer has been formed. As revealed by thermogravimetric analysis (TGA) (Supporting Information, Fig. S25), P(AB-3HT-borazine) polymer exhibits good thermal stability with a mass loss of 5 wt.% starting at 203 °C, and a loss of about 30 wt.% at 351 °C. On the other hands, DSC analysis performed from -25 to 200 °C showed a glass transition (T_g) at about 112 °C. Moreover, no melting...
and crystallization peaks were detected, suggesting the amorphous nature of the polymer (Supporting Information, Fig. S26).

**Figure 10.** $^1$H NMR spectrum of P(AB-3HT-borazine) polymer (CDCl$_3$, 500 MHz, 25 °C).

The absorption spectra of monomers bis-OTf-borazine 9, AB-3HT-(BPin)$_2$ 21 as well as P(AB-3HT-borazine) polymer in solutions and in thin films are depicted in **Figure 11**.

**Figure 11.** Normalized absorption spectra of monomers 9, 21 and P(AB-3HT-borazine) polymer in CHCl$_3$ solutions (a) and in thin films (b).

Absorption spectra of borazine unit either in solution or in film gave predominately one band at 268 nm and 266 nm, respectively, corresponding to $S_0$-$S_1$ transition. Absorption spectra of thiophene derivative unit 29 in solution showed two absorption maxima at 276 nm and 416 nm, corresponding to the $S_0$-$S_2$ and $S_0$-$S_1$ transitions, respectively. However, these bands are bathochromic shifted in the solid state. The P(AB-3HT-borazine)
polymer showed dual absorption bands. The high-energy band at around 268 nm develops from overlapped
maximum spectra of S₀-S₂ transitions of the borazine and the thiophene moieties, while, the low-energy band
(320-550 nm) is ascribed to the absorption of the thiophene derivative unit. Furthermore, no other bands have
been appeared at high wavelengths suggesting that no separate charge transfer occurred at the ground state. The
band gap (E_{opt}) of P(AB-3HT-borazine) polymer calculated from the absorption onsets (548 nm) in the solid
state is 2.27 eV, which is close to that of AB-3HT-(BPin) derivative (2.30 eV). Further, we have recorded
emission spectra of the monomers (9 and 21) and the polymer (P(AB-3HT-borazine)) in CHCl₃ (λ_{exc} = 268 nm,
276 nm and 416 nm, Fig. 12). A well-resolved peak at 330 nm corresponding to the S₁-S₀ transition was observed
when the borazine unit 9 is excited at 268 nm, whereas thiophene monomer 21 predominately gave two emission
maxima at 400 nm and 460 nm (λ_{exc} = 276 nm), attributing to S₂-S₀ and S₁-S₀ electronic transitions, respectively.
An emission maximum was obtained at 475 nm when excited at 416 nm, corresponding to S₂-S₀ electronic
transition. On the other hand, broad emission spectra were obtained when the polymer is excited at 268 nm and
276 nm, with a maximum at 330 nm. The broad nature of the spectra obtained for the polymer is attributed to the
contribution of the borazine and the thiophene moieties. The excitation of polymer at 416 nm gave a
weakly-emissive band between 560 nm and 550 nm. In addition to the broad nature of the fluorescence spectra,
the emission intensities are decreased compared to those of the reference borazine and thiophene derivatives
alone, suggesting the occurrence of an intramolecular charge-transfer (ICT).

![Figure 12](image)

Figure 12. Emission spectra of bis-OTf-borazine 9, AB-3HT-(BPin): 21 and P(AB-3HT-borazine) polymer
recorded at r.t. in CHCl₃ (λ_{exc} = 268 nm, 276 nm and 416 nm).

The photo-switching properties of the obtained P(AB-3HT-borazine) polymer was studied in CHCl₃ (0.025 g/L)
at r.t. When irradiated at the maximum absorption band (440 nm) no significant changes in the absorption band
were noticed (Fig. 13), suggesting that the polymer does not undergo any photo-induced switching process.
Considering that the band corresponding to the π-π* transition of the azo-group around 360 nm is veiled by the
intense S₀-S₁ transition band of the thiophene derivative unit, one can hypothesize that the lack of a selective
excitation of the azobenzene moieties is the main reason for the unsuccessful polymer switching. Also, it cannot be
excluded that an energy transfer from the excited state of the azobenzene to the oligothiophene could occur as
well, quenching the photoisomerization reaction.

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Figure 13. UV change in the absorption spectra of a 0.025 g/L solution of P(AB-3HT-borazine) polymer in CHCl₃ under irradiation at 440 nm at r.t.

The good solubility of the P(AB-3HT-borazine) polymer in a variety of organic solvents allowed a detailed study of its solvatochromic behavior. Thus, in order to get insight into the ICT nature of the P(AB-3HT-borazine) polymer, the solvent-dependent absorption and emission profiles (Fig. 14) were recorded in cyclohexane (dielectric permittivity \( \varepsilon = 2.02 \)), toluene (\( \varepsilon = 2.38 \)), THF (\( \varepsilon = 7.58 \)), CHCl₃ (\( \varepsilon = 4.81 \)), MeOH (\( \varepsilon = 32.7 \)), MeCN (\( \varepsilon = 37.5 \)) and DMSO (\( \varepsilon = 46.7 \)). A slight red shift was observed in the absorption band maxima accompanied by a broadening of the spectra when passing from nonpolar to polar solvents (Fig. 14a). However, changes in the emission spectra are more pronounced (Fig. 14b), with the polymer emitting at 660 nm and 720 nm. It is worthy to note that no significant differences were found between protic and aprotic solvents, suggesting that the hydrogen-bonding interaction is not responsible for the red shift. The significant solvent-induced fluorescence quenching could be explained either by an excited-state photo-induced intramolecular charge-transfer (ICT) or by internal energy transfer (IET) or even both phenomena taking place between the borazine and thiophene units.

Figure 14. Absorption (a) and emission (b) spectra of the P(AB-3HT-borazine) polymer in various solvents of different polarities (\( \lambda_{exc} = 416 \) nm).
Cyclic voltammetry (CV) was used to investigate the electrochemical properties of the polymer P(AB-3HT-borazine), along with that of its monomeric precursors bis-OTf-borazine 9 and AB-3HT-(BPin)2 21 in a solution of n-Bu4NPF6 (0.2 M) in CH2Cl2. As shown in Figure 15, the oxidation of borazine 9 is observed at a more anodic potential than that of the polymer and the thiophene 21. Its oxidation peak is observed around 1.6 V and its HOMO is determined at -5.8 eV from its onset oxidation potential Eonsetox measured at 1.4 V. No reduction was observed before the reduction of the electrolytic medium, suggesting that this borazine has a LUMO energy level higher than -1.9 eV. The CV recorded for the AB-3HT-(BPin)2 21, presents reversible oxidation and reduction processes with E1ox at 1.3 V and E1red at -1.39 V. From the Eonsetox/Eonsetred, the HOMO and LUMO energy levels of AB-3HT-(BPin)2 21 were determined to be at -5.58 eV and -3.17 eV, respectively, resulting in an electrochemical bandgap of 2.41 eV. The CV trace of the P(AB-3HT-borazine) polymer exhibited a weakly reversible oxidation (at a lowest potential value than that of the two precursors) and an irreversible reduction wave with E1ox at 1.24 V and E1red at -1.78 V, respectively. The HOMO and LUMO energy levels were calculated to be -5.36 eV and -3.08 eV, respectively, from their onset oxidation/reduction potential values. The electrochemical band gap was calculated to be 2.28 eV, which is slightly lower than that observed for the thiophene precursors, indicating a higher conjugation length in the polymer (see also the optical band gap of 2.27 eV).

Figure 15. Cyclic voltammograms (CV) recorded in CH2Cl2, n-Bu4NPF6 (0.2 M), using a platinum disk working electrode (Ø 1 mm) at a scan rate of 100 mV/s, Al2O3 was added to the electrolytic medium to remove water traces. CV traces of bis-OTf-borazine 9 in black, AB-3HT-(BPin)2 21 in red and polymer P(AB-3HT-borazine) in blue.

CONCLUSIONS

Owing to the possibility of functionalizing borazine cores with different groups on the aryl substituents at the N and B atoms, in this paper we reported the use of the borazine core as a modular scaffold to prepare photoactive hybrid BNC by means of the Pd-catalysed Suzuki cross-coupling reaction from the versatile tris-OTf-borazine derivative (4). Following this approach, we developed molecular BNC hybrid molecular scaffolds that, decorated with three azobenzene moieties, displayed reversible E/Z photoisomerization. The chemical structure was unveiled by X-ray diffraction analysis. The photoswitching properties of azo-borazine-3 have been investigated by means of UV/VIS spectroscopy and exhibits efficient reversible E/Z isomerization in toluene. To further
explore the chemical versatility of the borazine core, the new BN-doping polythiophene-type polymer P(AB-3HT-borazine) incorporating the borazine core, azobenzene and 3HT skeletons was also developed through Suzuki-type cross-coupling polycondensation reaction. Thermal, optical and electrochemical properties were investigated. In particular, emission studies in solvents of different polarity, suggested that the polymer undergoes intramolecular charge-transfer (ICT). This work opens the gate of applying the rapidly developing borazine chemistry as a new toolbox for engineering functional materials with tailored and exploitable optoelectronic properties.

EXPERIMENTAL SECTION

General Experimental Methods. Adsorption silica chromatography columns (SCC) were performed using Merck Gerduran silica gel 60 (particle size 40 - 60 μm). NMR spectra (1H, 13C NMR, 11B and 19F NMR) were recorded on a 400 MHz (Jeol JNM EX-400) or 500 MHz NMR (Jeol JNM ECZR-500) spectrometer. Chemical shifts are reported in parts per million (ppm) using the solvent residual signal as an internal reference (CDCl3 δH = 7.26 ppm, δC = 77.16 ppm; CD2Cl2 δH = 5.32 ppm, δC = 54.00 ppm; (CD3)2SO δH = 2.50 ppm, δC = 39.52 ppm).

For 11B, chemical shifts are reported in ppm downfield from BF3·OEt2 as internal reference, and analyses were performed in quartz tubes. Resonance multiplicity is described as s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), m (multiplet), br (broad signal), dd (doublet of doublets). Carbon spectra were acquired with a complete decoupling for the proton. All spectra were recorded at 25 °C unless specified otherwise. Infrared spectra (IR) were recorded on a Perkin-Elmer Spectrum II FTIR System UATR, mounted with a diamond crystal. Selected absorption bands are reported in wavenumber (cm⁻¹).

Emission studies in solvents of different polarity, suggested that the polymer undergoes intramolecular charge-transfer (ICT). This work opens the gate of applying the rapidly developing borazine chemistry as a new toolbox for engineering functional materials with tailored and exploitable optoelectronic properties.
merging two different data collections done on the same crystal, mounted with different orientations. The
diffraction data were indexed, integrated and scaled using XDS. The structures were solved by direct methods
implemented in the Sir2014 code. Fourier analysis and refinement were performed by the full-matrix
least-squares based on F² implemented in SHELXL-2018/3. The Coot program was used for modeling.
Anisotropic thermal motion was then applied to all atoms with occupancy greater than 75%. Hydrogen atoms
were included at calculated positions with isotropic U_factors = 1.2·U_eq or U_factors = 1.5·U_eq for methyl groups (U_eq
being the equivalent isotropic thermal factor of the bonded non hydrogen atom). Restraints on bond lengths, angles
and thermal motions (DFIX, DANG, SIMU and DELU) have been applied on disordered fragments. Essential
crystal and refinement data are reported in the supporting information document (Table S1). Size exclusion
chromatography (SEC or GPC) was performed in THF (with 2% triethylamine added) at 35 °C using a Polymer
Laboratories liquid chromatograph equipped with a PL-DG802 degasser, an isocratic HPLC pump LC 1120 (flow
rate = 1 mL.min⁻¹), a Marathon autosampler (loop volume = 200 μL, solution conc. = 1 mg.mL⁻¹), a PL-DRI
refractive index detector and three columns: a PL gel 10 μm guard column and two PL gel Mixed-B 10 μm
columns (linear columns for separation of MWPS ranging from 500 to 106 daltons). Poly(styrene) standards were
used for calibration. Cyclic voltammetry was recorded against saturated calomel electrode (SCE) in
CH₂Cl₂-ν-Bu₄NPF₆ (0.2 M) using a platinum disk working electrode (Ø 1.0 mm) at a scan rate of 100 mV.s⁻¹.
AλLi₂O₃ was added to the electrolytic medium to avoid any water traces. Chemicals were purchased from Sigma
Aldrich, Acros Organics, Fluorochem, TCI, VWR, carboxsynth, and ABCR, and were used as received, unless
otherwise stated. Solvents were purchased from Sigma Aldrich, Acros Organics and VWR, and deuterated
solvents were purchased from Eurisotop. THF was distilled from Na/benzophenone and stored on activated 3 Å
molecular sieves 24 hours prior to use and toluene were distilled from CaH₂ and stored on activated 3 Å molecular
sieves 24 hours prior to use. Aniline was purified by distillation from Sn powder, followed by distillation from Zn
powder, followed by distillation from CaH₂ under inert atmosphere, yielding a transparent colorless liquid stored
protected from light under argon. Anhydrous conditions, when necessary, were achieved by keeping all glassware
in the oven at 120 °C overnight and then allowed to cool down under a vacuum followed by drying the two-neck
flask by flaming with a heat gun under a vacuum and purging with N₂. The inert atmosphere was maintained using
N₂-filled balloons equipped with a syringe and needle that was used to penetrate the rubber stoppers used to close
the flask’s necks.

4-bromo-3,5-di-methylaniline (**5**). To a solution of distilled 3,5-di-methylaniline **4** (1.2 mL, 10 mmol) in
anhydrous DMF (10 mL) was added dropwise a solution of N-bromosuccinimide (NBS) (1.8 g, 10 mmol) in
anhydrous DMF (10 mL) at 0 °C. The reaction mixture was stirred at r.t. for 24 h. The crude is extracted with
CH₂Cl₂, and the organic phases are dried over MgSO₄ and evaporated yielding a brown solid, purified by column
chromatography (cyclohexane/EtOAc 0 to 20 %) to the desired product **5** as a white solid (1.6 g, 80%). Mp: 72.7
- 74.1 °C. ¹H NMR (CDCl₃, 400 MHz): δ 2.32 (s, 6 H), 3.54 (s, 2 H), 6.44 (s, 2 H). ¹³C{¹H} NMR (CDCl₃, 101
MHz): δ 24.0, 115.2, 116.0, 139.0, 145.1. FTIR (UATR) ν (cm⁻¹): 3403, 3307, 2953, 2916, 1623, 1586. HRMS
(EI-ToF) m/z: [M]⁺ Calcd for C₈H₁₀BrN⁺; 198.9997; Found, 198.9998.

N,N’-di-allyl-4-bromo-3,5-di-methylaniline (**6**) and N,N’-di-benzyl-4-bromo-3,5-di-methylaniline (**7**).
4-bromo-3,5-dimethylaniline (1.001 g, 5 mmol), NaHCO₃ (1.2605 g, 15 mmol) and sodium dodecyl sulfate (SDS)
(20 mg) were dispersed in a mixture of EtOH and H₂O (2:5 v/v) (30 mL). R-Br (R= Allyl or R= Bn) (1 mL, 11.6
mmol) was added dropwise to the mixture. The reaction was carried out at 80 °C for 16 h. The reaction mixture was diluted with CH₂Cl₂, washed with brine and water, dried over MgSO₄ and evaporated to yield brownish oil.

Column chromatography (cyclohexane) purification afforded the desired product 6' and 7' as transparent oil (1.34 g, 96%) and white solid (1.52 g, 80%), respectively.

\[ N,N' \text{-diallyl-4-bromo-3,5-dimethylaniline (6').} \]
\[ N,N' \text{-di-benzyl-4-bromo-3,5-di-methylaniline (7').} \]

\[ 11H NMR (CDCl₃, 400 MHz): \delta 2.43 (s, 6 H), 3.95 (m, 4 H), 5.22-5.26 (m, 4 H), 5.91 (m, 2 H), 6.52 (s, 2 H). \]
\[ 13C\{1H\} NMR (CDCl₃, 101 MHz): \delta 24.4, 52.8, 112.5, 114.1, 116.1, 133.8, 138.38, 147.4. \]

FTIR (UATR) \( \nu \) (cm\(^{-1}\)): 3078, 2917, 2979, 1642, 1588, 1476, 1376, 1417, 1279, 1199, 994, 918, 823, 737. HRMS (ESI-ToF) m/z: [M]+ Calcd for \( C_{14}H_{33}BrN^+ \), 279.0623; Found 279.0620.

\[ N,N' \text{-di-benzyl-4-bromo-3,5-di-methylaniline (7').} \]

\[ 1H NMR (CDCl₃, 400 MHz): \delta 2.29 (s, 6 H), 4.59 (s, 4 H), 6.49 (s, 2 H), 7.21 (m, 4 H), 7.35 (m, 6 H). \]
\[ 13C\{1H\} NMR (CDCl₃, 101 MHz): \delta 24.4, 54.0, 112.5, 114.6, 126.8, 127.1, 128.8, 138.4, 138.7, 148.0. \]

FTIR (UATR) \( \nu \) (cm\(^{-1}\)): 3026.59, 2917.93, 1591.86, 1200.17, 1073.88, 1026.88. HRMS (ESI-ToF) m/z: [M]+ Calcd for \( C_{22}H_{32}BrN^+ \), 379.0936; Found 379.0935.

\[ \text{Allyl-borazine (9')} \text{ and Benzyl-borazine (10').} \]

Following the general procedure for borazine synthesis\(^8\): aniline (0.28 mL, 3.0 mmol) was used in anhydrous toluene (8 mL) with BCl₃ (1 M in heptane, 2.7 mL, 2.64 mmol).

Ar-Li is prepared as nucleophile from \( N,N' \text{-di-allyl-4-bromo-3,5-di-methylaniline 6'} \) or \( N,N' \text{-di-benzyl-4-bromo-3,5-di-methylaniline 7'} \) (0.681 g, 2.42 mmol) in anhydrous THF (10 mL) with tert-BuLi (1.7 M in pentane, 2.92 mL, 4.96 mmol). The yellow suspension was stirred at r.t. for 16 h. Solvents were removed under reduced pressure giving brown solid. Precipitation in cold MeOH yielded the desired compound Allyl-borazine \( 9' \) and Benzyl-borazine \( 10' \) as white solids (0.32 g, 35%) and (0.84 g, 70%), respectively.

\[ \text{Allyl-borazine (9').} \]
\[ \text{Mp: 195.5-196.9 °C,} \text{ 1H NMR (CDCl₃, 400 MHz):} \delta 2.14 (s, 18 H), 3.65 (d, 12 H), 4.92-5.02 (q, 12 H), 5.65 (m, 6 H), 5.93 (s, 6 H), 6.67-6.75 (m, 15 H). \]
\[ 13C\{1H\} NMR (CDCl₃, 101 MHz): \delta 23.6, 52.4, 111.0, 115.9, 123.6, 126.5, 127.6, 134.7, 138.4, 146.9, 148.2. \]

Signal for carbon atom attached to boron atom is missing due to quadrupolar relaxation. \( 11B NMR (CDCl₃, 128 MHz): \delta 36.2 (br). \)

FTIR (UATR) \( \nu \) (cm\(^{-1}\)): 3024, 2913, 1642, 1598, 1491, 1350. HRMS (MALDI-ToF) m/z: [M]+ Calcd for \( C_{66}H_{50}B_{3}N_{6}^+ \), 906.5863; Found 906.5854.

\[ \text{Benzyl-borazine (10').} \]
\[ \text{Mp: 229.8-231.8 °C,} \text{ 1H NMR (CDCl₃, 400 MHz):} \delta 2.15 (s, 18 H), 4.35 (s, 12 H), 6.03 (s, 6 H), 6.87 (m, 15 H), 7.02-7.04 (m, 12 H), 7.19-7.28 (m, 18 H). \]
\[ 13C\{1H\} NMR (CDCl₃, 101 MHz): \delta 23.7, 53.8, 110.7, 124.1, 126.9, 127.1, 127.4, 128.67, 139.1, 139.5. \]

Signal for carbon atom attached to boron atom is missing due to quadrupolar relaxation. \( 11B NMR (CDCl₃, 128 MHz): \delta 36.1 (br). \)

FTIR (UATR) \( \nu \) (cm\(^{-1}\)): 3057, 1600, 1492, 1394, 1351, 1273, 1202, 1170, 1028, 964, 845, 728, 697. HRMS (ESI-ToF) m/z: [M+H]+ Calcd for \( C_{98}H_{52}B_{3}N_{6}^+ \), 1207.6875; Found 1207.6841.

\[ \text{Tri-amo-borazine (11').} \]

Benzyl-borazine (10') (797.7 mg, 0.66 mmol) was dissolved in a mixture of CH₂Cl₂ and MeOH (85:15 v/v) (30 mL). Pd(OH)₂/C (20 %, 161.1 mg, 1.14 mmol) was added to the solution. The suspension was hydrogenated with H₂ (1 atm) at r.t. for 24 h. The crude was filtrated on celite pad and evaporated to a brown residue purified on neutral alumina plug (MeOH) yielding tri-amo-borazine \( 11' \) as a white powder (0.42 g, 95 %). Mp: decomposition before melting around 150 °C.

\[ 1H NMR (CDCl₃, 400 MHz): \delta 2.19 (s, 18 H), 6.00 (s, 6 H), 6.67 (t, 3 H), 6.74 (t, 6 H), 6.86-6.88 (d, 6 H). \]
\[ 13C\{1H\} NMR (CDCl₃, 101 MHz): \delta 23.6, 114.8, \]

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125.1, 127.7, 128.4, 139.6, 146.6, 148.2. Signal for carbon atom attached to boron atom is missing due to quadrupolar relaxation. $^{11}$B NMR (CDCl$_3$, 128 MHz): $\delta$ 36.9 (br). FTIR (UATR) $\nu$ (cm$^{-1}$): 2913, 1599, 1491, 1491, 1452, 1355, 1307, 1074, 1026, 842, 746, 699. HRMS (ESI-ToF) m/z: [M]$^+$ Calcd for C$_{42}$H$_{32}$B$_3$N$_6$+, 666.3985; Found 666.4021. 

(4-bromo-3,5-dimethoxy)(tert-butyl)dimethylsilane (2). 4-bromo-3,5-dimethylphenol (6.28 g, 31.20 mmol) and imidazole (6.35 g, 93.3 mmol) were dissolved in DMF (80 mL) and tert-butylimidethylsilane (TBDMSCl) (6.6 g, 43.68 mmol) was added. The reaction was carried out at 50 °C and imidazole was cooled down to r.t. and extracted with CH$_2$Cl$_2$ (3 x 60 mL). The organic phase was stirred at r.t. for 15 h. The reaction mixture was cooled to r.t. and extracted with THF (3 x 50 mL). Purified by column chromatography (cyclohexane/CH$_2$Cl$_2$, 8:2 v/v) affording the desired compound 4 as a white powder (0.583 g, 75%). Mp: 236-238 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 2.32 (s, 18 H), 6.49 (s, 6 H), 6.75-6.77 (m, 6 H), 6.80-6.82 (m, 9 H). $^{13}$C ($^1$H) NMR (CDCl$_3$, 100 MHz): $\delta$ 23.2, 27.0, 118.1, 120.3, 125.5, 126.4, 127.5, 140.4, 144.8, 149.2. Signal for carbon atom attached to boron atom is missing due to quadrupolar relaxation.

Tri-B-(2,6-dimethyl-4-O-TBDMOS-phenyl)-tri-N-phenyl-borazine (3). Aniline (0.61 mL, 6.6 mmol) was used in anhydrous toluene (8 mL) with BCl$_3$ (1 M in heptane, 8 mL, 7.92 mmol). Ar-Li is prepared as nucleophile from 4-bromo-3,5-dimethoxy(tert-butyl)dimethylsilane 2 (2.46 g, 7.8 mmol) in anhydrous THF (20 mL) with tert-BuLi (1.7 M in pentane, 10.1 mL, 17.16 mmol). The yellow suspension was stirred at r.t. for 16 h. Solvents were removed under reduced pressure affording pale yellow solid. The mixture was poured in water (30 mL) and extracted with CH$_2$Cl$_2$ (3 x 30 mL). The organic phase was stirred at r.t. for 15 h. The precipitate was then filtered off and washed with THF (3 x 30 mL). The obtained solid was dried under vacuum affording pale yellow solid extracted with CH$_2$Cl$_2$ (3 x 50 mL). Purified by column chromatography (cyclohexane/CH$_2$Cl$_2$, 8:2 v/v) affording the desired compound 4 as a white powder (0.583 g, 75%). Mp: 236-238 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 2.32 (s, 18 H), 6.49 (s, 6 H), 6.75-6.77 (m, 6 H), 6.80-6.82 (m, 9 H). $^{13}$C ($^1$H) NMR (CDCl$_3$, 100 MHz): $\delta$ 23.2, 27.0, 118.1, 120.3, 125.5, 126.4, 127.5, 140.4, 144.8, 149.2. Signal for carbon atom attached to boron atom is missing due to quadrupolar relaxation. 

Tri-O2F-borazine (4). Tri-B-(2,6-dimethyl-4-O-TBDMOS-phenyl)-tri-N-phenyl-borazine 3 (736.1 mg, 0.73 mmol) was dissolved in anhydrous THF (20 mL). TBAF (1 M in THF, 0.8 mL, 0.803 mmol) was added dropwise at 0 °C, a white precipitate was formed in a yellowish solution. The reaction mixture was stirred at r.t. for 2 h. The precipitate was then filtered off and washed with THF (3 x 30 mL). The obtained solid was dried under vacuum and used in the followed step without further purification. The obtained off-white solid from the step one (478.8 mg, 0.71 mmol) was dissolved in pyridine (30 mL) and triflic anhydride (TF$_2$O) (12 eq., 1.6 mL, 8.52 mmol) was added dropwise at 0 °C. The brownish solution was stirred at r.t. for 15 h. Solvents were removed under reduced pressure giving brown solid extracted with CH$_2$Cl$_2$ (3 x 50 mL). Purified by column chromatography (cyclohexane/CH$_2$Cl$_2$, 8:2 v/v) affording the desired compound 4 as a white powder (0.583 g, 75%). Mp: 236-238 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 2.32 (s, 18 H), 6.49 (s, 6 H), 6.75-6.77 (m, 6 H), 6.80-6.82 (m, 9 H). $^{13}$C ($^1$H) NMR (CDCl$_3$, 100 MHz): $\delta$ 23.2, 27.0, 118.1, 120.3, 125.5, 126.4, 127.5, 140.4, 144.8, 149.2. Signal for carbon atom attached to boron atom is missing due to quadrupolar relaxation.
carbon atom attached to boron atom is missing due to quadrupolar relaxation. $^{19}$F NMR (CDCl$_3$, 376 MHz): δ -72.76 (s). $^{11}$B NMR (CDCl$_3$, 128 MHz): δ 35.7 (br). FTIR (UATR): ν (cm$^{-1}$) 2924, 1590, 1492, 1419, 1364, 1240, 1207, 1121, 1013, 946, 845, 813, 769, 702. HRMS (ESI-ToF) m/z: [M+H]$^+$ Calcd for C$_{43}$H$_{40}$B$_3$F$_7$N$_9$O$_5$S$_3^+$, 1066.2057; Found 1066.2067. Characterization is in accordance with data reported in the literature.

(E)-1-(4-iodophenyl)-2-phenyldiazene (7). Nitrosobenzene 5 (3.0 g, 28 mmol) and 4-iodoaniline 6 (6.13 g, 28.0 mmol) were dissolved in acetic acid (50 mL). The mixture was stirred at r.t. for 18 h. The reaction was quenched by water (100 mL) and the orange precipitate was filtered off and washed with water. The crude was purified by column chromatography (cyclohexane) affording the desired molecule 7 as an orange solid (7.0 g, 81%). Mp: 98.2-100.4 °C. $^1$H NMR (DMSO, 400 MHz): δ 7.59-7.62 (m, 3 H), 7.67-7.69 (m, 2 H), 7.89-792 (m, 2 H), 7.98-8.00 (m, 2 H). $^{13}$C ($^1$H) NMR (CDCl$_3$, 100 MHz): δ 97.8, 123.1, 124.6, 129.3, 131.5, 138.5, 152.0, 152.6. FTIR (UATR) ν (cm$^{-1}$): 3060, 3041, 2252, 1917, 1744, 1576, 1444, 1393, 1297, 1221, 1153, 1070, 1051, 1017, 928, 907, 834, 731, 705, 689, 627. HRMS (ESI-ToF) m/z: [M+H]$^+$ Calcd for C$_{12}$H$_{10}$N$_2$I$^+$, 308.9883; Found 308.9882.

(E)-1-phenyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)diazene (8). (E)-1-(4-iodophenyl)-2-phenyldiazene 7 (1.6 g, 5.2 mmol), B$_2$Pin$_2$ (1.98 g, 7.8 mmol), KOAc (1.02 g, 10.4 mmol) and [Pd(dpff)Cl$_2$]CH$_2$Cl$_2$ (0.1272 g, 0.156 mmol) were suspended in anhydrous DMF (degassed by 3 freeze-pump-thaw cycles) (20 ml). The reaction was carried out under argon at 90 °C for 18 h. After cooling down to r.t., the reaction mixture was diluted with CH$_2$Cl$_2$ (60 mL), washed with brine and H$_2$O, dried over MgSO$_4$ and evaporated to a brown dark orange solid purified by column chromatography (cyclohexane/CH$_2$Cl$_2$, from 0 to 20%) yielding the desired compound 8 as an orange solid (1.3 g, 80%). Mp: 93.5-94.7 °C. $^1$H NMR (CDCl$_3$, 400 MHz): δ 1.36 (s, 12 H), 7.51-7.56 (m, 3 H), 7.88-7.95 (m, 6 H). $^{13}$C ($^1$H) NMR (CDCl$_3$, 100 MHz): δ 25.0, 84.2, 84.5, 122.3, 123.3, 129.5, 131.7, 135.9, 153.1, 154.7. $^{11}$B NMR (CDCl$_3$, 128 MHz): δ 29.6 (s). FTIR (UATR) ν (cm$^{-1}$): 3039, 2915, 1598, 1546, 1467, 1444, 1397, 1357, 1332, 1305, 1140, 1088, 1000, 963, 855. HRMS (ESI-ToF) m/z: [M+H]$^+$ Calcd for C$_{18}$H$_{22}$BN$_2$O$_4$, 309.1769; Found 309.1773.

Azoborane-3. Tris-OtF-borazine 4 (295.5 mg, 0.277 mmol), K$_2$CO$_3$ (462.0 mg, 3.328 mmol), compound 8 (341.9 mg, 1.114 mmol) and [Pd(PPh$_3$)$_2$] (19.2 mg, 16.6 x 10$^{-3}$ mmol) were suspended in a mixture of 1,4-dioxane and water (3:1 v/v) (16 mL) (degassed with 5 freeze-pump-thaw cycles) in a flame-dried 50-mL Schlenk flask. The reaction was carried out at 105 °C for 18 h. The reaction mixture was cooled down to r.t., diluted with CH$_2$Cl$_2$ (100 mL), filtrated on celite, washed with brine (100 mL) and H$_2$O (3 x 100 mL). The organic phase was dried over MgSO$_4$. The crude was purified by column chromatography (cyclohexane/CH$_2$Cl$_2$, from 0 to 10%) affording the desired compound azo-borane-3 as an orange solid (0.267 g, 83%). Mp: 270-272 °C. $^1$H NMR (CDCl$_3$, 400 MHz): δ 2.47 (s, 18 H), 6.80-6.84 (t, 3 H), 6.88-6.91 (t, 6 H), 6.97 (s, 6 H), 7.03-7.05 (d, 6 H), 7.46-7.55 (m, 9 H), 7.60-7.62 (d, 6 H), 7.88-7.92 (m, 12 H). $^{13}$C ($^1$H) NMR (CDCl$_3$, 100 MHz): δ 25.0, 84.2, 93.9, 122.1, 122.9, 123.0, 123.1, 123.1, 123.6, 128.0, 129.2, 129.2, 129.3, 131.1, 131.3, 135.8. Signal for carbon atom attached to boron atom is missing due to quadrupolar relaxation. $^{11}$B-NMR (CDCl$_3$, 128 MHz): δ 35.98 (br). FTIR (UATR) ν (cm$^{-1}$): 3039, 2915, 1598, 1546, 1490, 1454, 1422, 1353, 1305, 1292, 1223, 1154, 1072, 1011, 838, 792. HRMS (MALDI-ToF) m/z: [M+H]$^+$ Calcd for C$_{78}$H$_{67}$B$_3$N$_9$O$_2$S$^+$, 1162.5793; Found 1162.6010.
Tris-OTf-borazine (9). Tris-OTf-borazine 4 (200.5 mg, 0.202 mmol), K$_2$CO$_3$ (33.6 mg, 0.242 mmol), phenylboronic acid (8.2 mg, 67 x 10^{-3} mmol) and [Pd(PPh$_3$)$_4$] (7.2 mg, 6.06 x 10^{-3} mmol) were suspended in a mixture of 1,4-dioxane and water (3:1, v/v) (12 mL) degassed with 5 freeze-pump-thaw cycles in a flame-dried 50-mL Schlenk flask. The reaction was carried out at 105 °C for 8 h. The reaction mixture was cooled down to r.t., diluted with CH$_2$Cl$_2$ (100 mL), filtered on celite, washed with brine (100 mL) and H$_2$O (3 x 100 mL). The organic phase was dried over MgSO$_4$, evaporated to a brownish solid and purified by column chromatography (cyclohexane/CH$_2$Cl$_2$, from 0 to 10%) yielding the desired compound 9 as a white solid (0.06 g, 30%). Mp: 180.4-182.2 °C. 1H NMR (CD$_2$Cl$_2$, 400 MHz): δ 2.33 (s, 18 H), 6.49 (s, 4 H), 6.75-6.83 (m, 17 H), 7.21 (t, 1 H), 7.30 (t, 2 H), 7.38-7.40 (d, 2 H). 13C{[1]H} NMR (CDCl$_3$, 101 MHz): δ 23.3, 23.4, 118.0, 124.4, 125.1, 125.3, 126.5, 126.7, 126.8, 126.9, 127.3, 127.5, 128.6, 138.0, 139.8, 140.4, 141.2, 145.1, 145.3, 149.2. 19F NMR (CDCl$_3$, 376 MHz): δ -72.75. 11B NMR (CDCl$_3$, 128 MHz): δ 35.2 (br). FTIR (UATR) ν (cm$^{-1}$): 3040, 2923, 2854, 1590, 1492, 1454, 1419, 1363, 1310, 1240, 1208, 1142, 1120, 1075, 1013, 945, 908, 869, 845, 794, 749, 701, 582. HRMS (MALDI-ToF) m/z: [M]+ Calcd for C$_{30}$H$_{45}$B$_{3}$N$_{17}$F$_{3}$O$_{3}$S$_{2}$+; Found 994.2969; Found 994.3002.

1-nitro-2-(oct-1-ynyl)benzene (11). 1-bromo-2-nitrobenzene 10 (2.5 g, 12.5 mmol), 1-octyne (1.73 g, 2.4 mL, 12.5 mmol), [Pd(PPh$_3$)$_4$] (288 mg, 0.25 mmol) and CuBr (73 mg, 0.5 mmol) were dissolved in a freshly distilled and degassed with 3 freeze-pump-thaw cycles Et$_2$N (50 mL) a flame-dried 100-mL Schlenk flask. The reaction was carried out at 90 °C under argon atmosphere for 15 h. The reaction mixture was cooled down to r.t., diluted with 300 mL of Et$_2$O, washed with a saturated solution of NH$_4$Cl (3 x 100 mL) and water (3 x 100 mL), dried over MgSO$_4$, and evaporated to a dark oil. The crude product was purified by column chromatography (n-heptane/EtOAc, from 0 to 20%) yielding the desired compound 11 as a brownish oil (2.6 g, 90%). 1H NMR (CD$_2$Cl$_2$, 500 MHz): δ 0.89 (t, 3 H), 1.29-1.34 (m, 4 H), 1.46 (m, 2 H), 1.62 (m, 2 H), 2.45 (t, 2 H), 7.36 (t, 1 H), 7.49 (t, 1 H), 7.54 (d, 1 H), 7.92 (d, 1 H). 13C{[1]H} NMR (CDCl$_3$, 126 MHz): δ 14.1,19.9, 22.6, 28.4, 28.6, 31.4, 76.0, 99.5, 119.4, 124.4, 127.9, 132.6, 134.8, 150.1. FTIR (UATR) ν (cm$^{-1}$): 2954, 2928, 2858, 2228, 1608, 1568, 1524, 1480, 1466, 1439, 1429, 1262, 851, 783, 744, 655. LRMS (EI-ToF) m/z: [M]+ Calcd for C$_{13}$H$_{23}$NO$_2^-$, 231.1259; Found 231.131. Characterization is in accordance with data reported in the literature. 1-octyne (1.73 g, 2.4 mL, 12.5 mmol) was added dropwise over 50 min to 2-octylaniline 12 (1.50 g, 7.3 mmol) in THF (50 mL). After completion of the addition, the solution was stirred at r.t. for 1 h. The solution was filtered to remove the formed pyridinium hydrobromide salt. Then, the solution was treated with a saturated solution of NaHCO$_3$ (3 x 100 ml) to remove any excess of bromide, washed with water (3 x 100 mL), dried over MgSO$_4$ and evaporated to a dark oil. The
crude product was purified by column chromatography (n-heptane/ EtOAc, from 0 to 30%) yielding the desired compound 13 as a brownish oil (1.47 g, 71%). 1H NMR (CDCl3, 500 MHz): δ 0.91 (t, 3 H), 1.30-1.42 (m, 10 H), 1.60 (m, 2 H), 2.43 (t, 2 H), 3.61 (s, 2 H), 6.53 (d, 1 H), 7.11-7.12 (dd, 1 H), 7.15 (d, 1 H). 13C{1H} NMR (CDCl3, 100 MHz): δ 13.2, 21.8, 27.5, 28.3, 28.6, 28.7, 30.2, 31.0, 109.4, 116.0, 128.2, 128.5, 130.9, 142.2. FTIR (UATR) ν (cm⁻¹): 3475, 3387, 2953, 2853, 1619, 1488, 1409, 1278, 1077. MS (GC-MS) m/z: [M]+ Calcd for C14H22BrN+. 283.0936; Found 283.12. Characterization is in accordance with data reported in the literature.40

2-octyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (14). 4-bromo-2-octylaniline 13 (1.32 g, 4.62 mmol), B3Pin2 (1.41 g, 5.54 mmol), KOAc (1.36 g, 13.86 mmol) and [Pd(dppf)Cl2]2CH2Cl2 (100 mg, 0.14 mmol) were suspended in 1,4-dioxane (degassed by 3 freeze-to-thaw cycles) (45 mL). The reaction was carried out at 85 °C for 16 h. After cooling down to r.t. the reaction mixture was diluted with EtOAc (100 mL), filtered over celite, washed with brine (2 x 100 mL) and H2O (3 x 100 mL), dried over MgSO4 and evaporated to black oil. The crude product was purified by column chromatography (EtOAc/n-heptane, from 0 to 20%) yielding the molecule 14 as a brownish oil (0.765 g, 50%). 1H NMR (CDCl3, 500 MHz): δ 0.88 (t, 3 H), 1.26-1.32 (m, 22 H) (integration 34 H for is due to the presence of pinacolborane 12H), 1.61 (m, 2 H), 2.49 (t, 2 H), 3.81 (s, 2 H), 6.64-6.66 (d, 1 H), 7.49 (m, 2 H). 13C{1H} NMR (CDCl3, 101 MHz): δ 14.2, 22.8, 25.1, 29.0, 29.4, 29.6, 30.0, 31.5, 32.0, 77.0, 77.6, 77.7, 83.3, 83.6, 114.7, 125.8, 134.2, 136.5, 147.4. 11B NMR (CDCl3, 128 MHz): δ 29.4 (s). FTIR (UATR) ν (cm⁻¹): 3473, 3365, 2925, 2825, 1621, 1605, 1418, 1353, 1325, 1303, 1165, 1123, 1106, 1090, 964, 856. HRMS (ESI-ToF) m/z: [M+H]+ Calcd for C20H32BNO3+, 332.2755; Found 332.2760. Characterization is in accordance with data reported in the literature.40

3-Hexyl-2,5-diiodothiophene (16). A solution of N-Iodosuccinimide (NIS) (14.04 g, 62.4 mmol) in CHCl3 (30 mL) was added dropwise to a solution of 3-hexylthiophene 15 (5.3 mL, 29.71 mmol) in a mixture of acetic acid and CHCl3 (30:10 mL). The reaction mixture was stirred in dark at r.t. for 24 h. The reaction mixture was diluted with CH2Cl2 (100 mL), quenched with a saturated solution of Na2S2O3 (50 mL), washed with H2O (3 x 100 mL), dried over MgSO4 and evaporated to light pink oil. The crude product was purified by column chromatography (cyclohexane) affording the desired compound 16 as a colorless oil (11.2 g, 90%). 1H NMR (CDCl3, 400 MHz): δ 0.92 (t, 3 H), 1.32 (m, 6 H), 1.55 (m, 2 H), 2.50 (t, 2 H), 6.90 (s, 1 H). 13C{1H} NMR (CDCl3, 101 MHz): δ 14.3, 22.7, 28.9, 30.0, 31.7, 32.1, 76.1, 77.2, 137.8, 149.5. FTIR (UATR) ν (cm⁻¹): 2953, 2923, 2853, 1525, 1464, 1395, 1190, 982, 907, 827, 724, 695, 649, 468. HRMS (ESI-ToF) m/z: [M+H]+ Calcd for C10H13I2S+, 420.8978; Found 420.8961. Characterization is in accordance with data reported in the literature.40

(4,4′-(3-hexylthiophene-2,5-diyl)bis(2-octylaniline) (17). 2-octyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline 14 (520.1 mg, 1.6 mmol), 3-hexyl-2,5-diiodothiophene 16 (300.2 mg, 0.71 mmol) and K2CO3 (790 mg, 5.72 mmol) were dissolved in a mixture of 1,4-dioxane and H2O (9:3 v/v) (12 mL). The reaction mixture was degassed by three freeze-pump-thaw cycles. Then, [Pd(PPh3)4] (46.2 mg, 0.04 mmol) was added. The reaction was carried out at 105 °C for 24 h. The mixture was cooled down to r.t., diluted with CH2Cl2 (50 mL), filtered over celite, washed with brine (2 x 100 mL) and water (2 x 100 mL), dried over MgSO4, evaporated and purified by column chromatography (cyclohexane/EtOAc, from 0 to 10%) yielding the desired compound 17 as yellow viscous oil (0.122 g, 30%). 1H NMR (CDCl3, 500 MHz): δ 0.89-0.90 (t, 9 H), 1.30-1.45 (m, 24 H), 1.66 (m, 6H), 2.52 (t, 4 H), 2.63 (t, 2 H), 3.70...
(s, 4 H), 6.68 (q, 2 H), 7.03 (s, 1 H), 7.13 (s, 2 H), 7.28-7.30 (m, 2 H). 13C{1H} NMR (CDCl3, 101 MHz): δ 14.2, 22.8, 22.8, 28.8, 28.9, 29.2, 29.4, 29.5, 29.7, 29.7, 29.8, 29.9, 31.2, 31.4, 31.5, 31.9, 32.0, 115.5, 115.9, 123.8, 124.4, 125.4, 125.8, 126.9, 127.0, 127.3, 127.8, 130.4, 136.5, 138.4, 141.9, 143.4, 143.6. FTIR (UATR) ν (cm⁻¹): 3380, 2954, 2923, 2853, 1619, 1497, 1464, 1377, 1283, 1156, 907, 816, 732, 646, 532. LRMS (ESI-ToF) m/z: [M+H]+ Calcd for C38H50N2S2: 575.4393; Found 575.4331. Characterization is in accordance with data reported in the literature.40

1-bromo-4-nitrosobenzene (19). A solution of Oxone® (7.2 g, 11.7 mmol) in water (48 mL) was added to a solution of freshly recrystallized 4-bromoaniline (1.04 g, 5.84 mmol) in CH2Cl2 (12 mL). The mixture was stirred at r.t. for 4 h. The reaction mixture was extracted with CH2Cl2 (3 x 20 mL) to give the desired compound 19 as a pale green solid that was used in the next step without further purification (2.15 g, quant.). 1H NMR (CDCl3, 400 MHz): δ 7.78 (s, 4 H).

(1E,1′E)-2,2′-((3-hexylthiophene-2,5-diyl)bis(2-octyl-4,1-phenylene))bis(1-(4-bromophenylene)diazene) (20). 1-bromo-4-nitrosobenzene 19 (2.14 g, 11.51 mmol) and compound 17 (1.51 g, 2.63 mmol) were dissolved in a mixture of AcOH and EtOAc (1:1 v/v) (40 mL). The reaction mixture was stirred at 45 °C for 36 h. The mixture was cooled down to r.t., diluted with CH2Cl2 (50 mL), washed with water (3 x 100 mL), dried over MgSO4, evaporated and purified by column chromatography (cyclohexane/CH2Cl2 from 0 to 30%) yielding the desired compound 20 as a viscous orange oil (1.08 g, 45%). 1H NMR (CDCl3, 500 MHz): δ 0.87 (t, 9 H), 1.25-1.42 (m, 26 H), 1.71 (m, 6 H), 2.75 (t, 2 H), 3.14-3.19 (q, 4 H), 7.34 (s, 1 H), 7.39-7.41 (dd, 1 H), 7.48 (d, 1 H), 7.52-7.54 (dd, 1 H), 7.60 (d, 1 H), 7.65-7.67 (m, 4 H), 7.72-7.75 (d, 2 H), 7.79-7.82 (m, 4 H). 13C{1H} NMR (CDCl3, 126 MHz): δ 14.2, 14.3, 22.8, 22.8, 29.4, 29.4, 29.6, 29.6, 29.7, 31.2, 31.6, 31.8, 31.8, 32.0, 32.3, 32.4, 115.8, 116.2, 123.8, 124.5, 124.6, 125.2, 125.3, 127.1, 127.3, 127.4, 131.1, 132.5, 132.5, 133.1, 137.7, 137.8, 141.1, 142.1, 143.8, 144.4, 149.2, 149.3, 151.9, 152.0. FTIR (UATR) ν (cm⁻¹): 2953, 2922, 2853, 1905, 1596, 1574, 1476.67, 1453, 1411, 1377, 1297, 1260, 1222, 1185, 1149, 1117, 1066, 1007, 886, 832, 722, 704. HRMS (ESI-ToF) m/z: [M+H]+ Calcd for C59H83Br3N2S2: 909.3135; Found 909.3126.

(1E,1′E)-2,2′-((3-hexylthiophene-2,5-diyl)bis(2-octyl-4,1-phenylene))bis(1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)diazene) (AB-3HT-(BPin)) (21). Compound 20 (1.00 g, 1.11 mmol), B2Pin2 (1.12 g, 4.41 mmol), KOAc (0.6477 g, 6.6 mmol) and [Pd(dpff)Cl2]2-CH2Cl2] (54 mg, 0.066 mmol) were suspended in 1,4-dioxane (degassed by 3 freeze-to-thaw cycles) (45 mL). The reaction was carried out at 90 °C for 24 h. After cooling down to r.t. the reaction mixture was diluted with CH2Cl2 (100 mL), filtered over celite to remove the Pd catalyst, washed with brine (2 x 100 mL) and H2O (3 x 100 mL), dried over MgSO4 and evaporated to a black oil purified by column chromatography (cyclohexane/CH2Cl2 from 0 to 10%) to yield the desired compound 21 as an orange viscous oil (0.72 g, 65%). 1H NMR (CDCl3, 400 MHz): δ 0.87 (t, 9 H), 1.27-1.38 (m, 50 H), 1.73 (m, 6 H), 2.75 (t, 2 H), 3.18 (q, 4 H), 7.34 (s, 1 H), 7.40-7.42 (dd, 1 H), 7.49 (d, 1 H), 7.53-7.55 (dd, 1 H), 7.61 (d, 1 H), 7.73-7.76 (m, 2 H), 7.89-7.92 (m, 4 H), 7.96-7.99 (m, 4 H). 13C{1H} NMR (CDCl3, 100 MHz): δ 14.2, 14.2, 22.8, 22.8, 25.0, 25.2, 27.0, 27.1, 29.4, 29.4, 29.4, 29.6, 29.6, 29.7, 29.7, 30.3, 31.2, 31.8, 32.0, 32.3, 32.4, 43.6, 83.6, 84.2, 84.2, 115.8, 116.1, 122.2, 123.7, 127.0, 127.3, 131.1, 135.8, 135.8, 137.0, 137.6, 138.1, 141.0, 142.1, 143.7, 144.4, 149.5, 149.6, 155.0, 155.1. Signals for the two carbon atoms attached to boron atoms are missing due to quadrupolar relaxation. 11B NMR (CDCl3, 128 MHz): δ 29.3 (s). FTIR (UATR) ν (cm⁻¹): 2923, 2853,
1599, 1571, 1480, 1396, 1324, 1272, 1216, 1186, 1124, 1086, 1014, 962, 886, 858, 848, 830, 736, 668, 653, 578, 540. HRMS (ESI-ToF) m/z: [M+H]^+ Calcd for C_{62}H_{87}B_{2}N_{4}O_{4}S^+, 1005.6668; Found 1005.6706.

**P(AB-3HT-borazine) polymer.** Bis-OTf-borazine 9 (100.00 mg, 0.1 mmol), compound 21 (101.06 mg, 0.1 mmol), K$_2$CO$_3$ (1.66 g, 1.2 mmol) were suspended in a mixture of toluene and water (2:0.2 v/v). The reaction mixture was degassed by three freeze-pump-thaw cycles. Then, [Pd(PPh$_3$)$_4$] (17.33 mg, 0.015 mmol) was added. The reaction was vigorously stirred at 100 °C for 48 h. The deep-orange reaction mixture turned gradually into brown accompanied with the precipitation of a black solid. P(AB-3HT-borazine) polymer was obtained by purification via Soxhlet extraction for 12 h using CHCl$_3$ followed by precipitation in MeOH. The orange-like polymer was finally dried under reduced pressure at 50 °C for 24 hours in 60% yield. Size exclusion chromatography (SEC) relative to polystyrene standard in THF (+2% Et$_3$N) at 30 °C: M$_n$ = 13.2 kDa, M$_w$ = 25.0 kDa, D$_{rel}$ = 1.92, DP = 9.

$^1$H NMR (CDCl$_3$, 500 MHz): δ 0.86 (br, 9 H), 1.25-1.40 (br, 50 H), 1.71 (s, 6 H), 2.17 (s, 6 H), 2.41-2.43 (br, 12 H), 2.74 (s, 2 H), 3.17 (s, 4 H), 6.75 (s, 1 H), 6.82 (s, 4 H), 6.92 (s, 15 H), 7.22 (s, 1 H), 7.31 (br, 4 H), 7.41 (s, 2 H), 7.47 (s, 1 H), 7.58 (br, 6 H), 7.72 (br, 2 H), 7.89 (s, 4 H).
ASSOCIATED CONTENT

Supporting Information

Synthetic schemes, copies of NMR spectra and thermal characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

CCDC 1906843, 1906842 and 1906844 contain the supplementary crystallographic data for compounds 3, Azo-borazine-3 and 4. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures.

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