NJC

New Journal of Chemistry

A journal for new directions in chemistry

Volume 36 | Number 5 | May 2012 | Pages 1123-1286

www.rsc.org/njc



ISSN 1144-0546

RSCPublishing



COVER ARTICLE Stolar and Baumgartner Synthesis and unexpected halochromism of carbazole-functionalized dithienophospholes

PAPER

Cite this: New J. Chem., 2012, 36, 1153–1160

Synthesis and unexpected halochromism of carbazole-functionalized dithienophospholes

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Received (in Montpellier, France) 10th January 2012, Accepted 14th February 2012 DOI: 10.1039/c2nj40022g

A series of π -conjugated donor-acceptor (D/A) chromophores using dithieno[3,2-*b*:2',3'-*d*]phosphole oxide as an acceptor and 3,6-carbazole as a donor component have been synthesized and characterized. The studies involved several molecular species with D–A, A–D–A, D–A–D architecture, as well as a polymeric species (D–A)_n. The different photophysical properties of the systems can be attributed to the carbazole unit *de facto* acting as aniline species for the π -conjugated system. Treatment of the donor-acceptor materials with acids resulted in the significant red shift of the absorption and emission wavelengths and the process was found to be reversible. Investigations *via* Density-Functional Theory (DFT) calculations revealed the nature of the unexpected red shift upon protonation.

Introduction

Organic π -conjugated materials are increasingly gaining attention due to their exceptional utility for practical applications in organic electronics such as Organic Light-Emitting Diodes (OLEDs), Organic Field-Effect Transistors (OFETs), and Organic Photovoltaics (OPVs), but also as highly sensitive chromophores in the area of molecular sensing.^{1,2} A major strength of organic materials is their highly versatile tunability that allows tailoring the materials' properties using a simple building block approach. Recent research has shown that the incorporation of heteroelements—main group elements such as B, Si, and P in particular—can also be used to efficiently tailor the properties of π -conjugated materials.³ Remarkably, this approach can lead to unique properties due to the intrinsic electronics and chemistry of these elements, which are not accessible using purely carbon-based building blocks.

A particularly intriguing strategy toward highly desirable photophysics involves the combination of donor- (D) and acceptor- (A) building blocks within the same π -conjugated scaffold.^{1,2} The electron-rich nature of the donor commonly increases the energy of the Highest Occupied Molecular Orbital (HOMO), while the electron-poor nature of the acceptor concurrently lowers the Lowest Unoccupied Molecular Orbital (LUMO). This leads to very narrow energy gaps for comparatively small chromophores. Furthermore, the intrinsic electronics of the donor/acceptor units provide an excellent opportunity for stimulus-responsive behavior of the system, as these functional groups can easily react with electrophiles and nucleophiles, respectively.²

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Reaction with either the donor or the acceptor component will result in an increased energy gap, which can translate into altered photophysics or electronics for the system, and is thus a desirable feature for the design of sensory materials. While the sensing of anions (*e.g.*, F^- and CN^-) can be accomplished with electron-deficient units such as organoboron species,^{3b} the detection of cationic or electron deficient species (Lewis acids, H^+) requires electron rich sites; nitrogen-based chromophores have a proven utility for such a purpose due to their pronounced basicity.⁴

Our comprehensive studies, using the dithieno [3,2-b:2',3'-d]phosphole system over the past eight years or so, have revealed that this unit shows exceptionally strong photoluminescence properties and is highly tunable through simple modification at the phosphorus center.⁵ More importantly, others and we could establish that the oxidation of the phosphorus center significantly enhances the electron-acceptor character of phosphole-based systems.⁶ In combination with appropriate donor groups, we were able to access a variety of molecular dithienophosphole chromophores with photoluminescence emissions that cover the full optical spectrum.^{5c} Moreover, using the 2,6-bis(dimethylaniline) functionalized dithienophosphole I (Scheme 1), we could show that protonation of the nitrogen centers significantly blue-shifts the emission color of the system from orange ($\lambda_{em} = 601 \text{ nm}$) to green ($\lambda_{\rm em}$ = 524 nm), which we could then use for the generation of white-light emission in combination with a suitable blue dithienophosphole chromophore.⁷

Inspired by these initial results, we set out to further study N-donor-functionalized dithienophospholes and their halochromic behavior in more detail. In this contribution we now report our systematic studies on such systems using 3(6)-carbazole as the donor component⁸ for the dithienophosphole acceptor system. The 3(6)-carbazole isomer was chosen because it provides



Scheme 1 A halochromic dithienophosphole.

optimal conjugation of the nitrogen center with the π -conjugated scaffold, and access to larger extended oligomers/polymers that allows for the investigation of the potential communication between building block chromophores.

Results and discussion

Synthesis and properties of the neutral carbazole-functionalized dithienophospholes

To gain some deeper insight into the photophysics and halochromism of this system, we have targeted molecular chromophores with A–D, D–A–D and A–D–A architecture, as well as a polymeric material $(A-D)_n$. The synthetic strategy towards these four different species followed established procedures using either mono- or difunctionalized building blocks, with a Suzuki–Miyaura cross-coupling as the central linking step. The mono- and dibrominated dithienophosphole derivatives 1⁹ and 2^{5c} were reported by us earlier. The 3-borylated carbazole 3 had also been reported in the literature before.¹⁰ The synthesis of the 3,6-diborylated carbazole 4 was adapted from the literature, involving N-alkylation of 3,6-dibromocarbazole and subsequent borylation with isopropoxypinacolborane after lithiation with *n*-BuLi at -78 °C in THF (Scheme 2).

With the necessary building blocks in hand, we then proceeded with the synthesis of the four targeted chromophores **5–8** in a standard Suzuki–Miyaura protocol in refluxing THF for 72 h using Pd(PPh₃)₄ as catalyst and CsF as base (Scheme 3). After column chromatography, or precipitation into methanol for the polymer, the corresponding chromophores could be isolated as orange/red solids in moderate yields, respectively. Multinuclear (¹H, ¹³C, ³¹P)



Scheme 2 Synthesis of the diborylated carbazole 4.



Scheme 3 Synthesis of the donor-acceptor chromophores.

NMR spectroscopy as well as high-resolution mass spectrometry confirmed the identity of the compounds.

The photophysics of the four chromophores exhibited some interesting features that revealed the electronic communication within the different species. UV-vis absorption as well as fluorescence emission showed two sets of spectra with similar maxima, one for **5** (A–D) and **7** (A–D–A) with $\lambda_{abs} \approx 420$ and $\lambda_{em} \approx 515$ nm, and one for **6** (D–A–D) and polymer **8** with $\lambda_{abs} \approx 455$ and $\lambda_{em} \approx 563$ nm (Table 1 and Fig. 1).

From these data it is clear that the 3,6-carbazole unit does not strongly promote extended conjugation throughout its scaffold, as anticipated, and basically only functions as an *p*-aniline component to the overall chromophore.¹¹ In addition, the incorporation of the nitrogen center in the aromatic framework reduces its donor character for the dithienophosphole acceptor to some extent, which is evident in the stronger red-shifted data for the reported bis(dimethylaniline) species I (cf.: $\lambda_{abs} = 524$ nm; $\lambda_{\rm em}$ = 601 nm). However, the large Stokes shifts and low photoluminescence quantum yields of 93 nm ($\phi_{\rm PL} = 0.20$) for **5**, 85 nm ($\phi_{PL} = 0.21$) for **7**, 107 nm ($\phi_{PL} = 0.15$) for **6** and 113 nm ($\phi_{PL} = 0.06$) for 8 clearly support the presence of charge-transfer processes involving non-radiative relaxation pathways within the chromophores that are more pronounced in the latter two species, in line with the contribution of two donor units.²

Acid response of the chromophores

To investigate the halochromic behavior of the four new chromophores, $CHCl_3$ solutions of the compounds were treated with *p*-toluenesulfonic acid (TsOH) to provide for a homogenous environment. Remarkably however, a very large excess of acid (*ca.* 100 equiv.) is required to induce a shift in the photophysics of the chromophores. This observation is in line with our earlier studies and was first attributed to the reduced

 Table 1
 Photophysical data and calculated frontier orbital energies for compounds 5–8 and their protonated congeners

Compound	$\lambda_{abs}{}^a/nm$	$\varepsilon_{\rm max}{}^a/{\rm L}~{\rm mol}^{-1}~{\rm cm}^{-1}$	$\lambda_{\rm ex}{}^b/{\rm nm}$	$\lambda_{\rm em}{}^b/{\rm nm}$	$\phi_{ ext{PL}}{}^c$	$E_{\rm HOMO}^{d}/{\rm eV}$	E_{LUMO}^{d}/eV	$\Delta E_{ m bg}{}^d/ m eV$
5	417	13 160	423	516	0.20	-5.12	-1.81	3.31
6	457	24 960	455	562	0.15	-4.83	-1.77	3.06
7	421	33 830	427	512	0.21	-5.13	-1.91	3.22
8	454	_	450	563	0.06	_	_	_
5(+)	427	11 880	432	580	0.08	-5.77	-3.33	2.44
6(+)	465	22 360	457	583	0.06	-5.59	-3.28	2.31
7(+)-mono			_	_	_	-5.50	-3.35	2.15
7(+)-di	428	29 650	433	572	0.08	-6.50	-3.86	2.64
8(+)	463	—	503	624	0.02	—	—	—

^{*a*} UV-Vis absorption in CHCl₃. ^{*b*} Fluorescence excitation and emission maxima in CHCl₃. ^{*c*} Photoluminescence quantum yield in CHCl₃ solution, relative to quinine sulfate (10⁻⁴ M in 0.1 M H₂SO₄). ^{*d*} Calculated energies, B3LYP/6-31G(d); a PCM solvation model (CHCl₃) used for cationic species.



Fig. 1 Photophysics of **5–8** in CHCl₃. Top: normalized absorption; bottom: normalized emission.

basicity of the nitrogen lone pair due to its incorporation within the π -conjugated system.⁷ As mentioned in the introduction, protonation of the nitrogen centers would result in a blue shift due to the elimination of the donor-component. However, the most striking observation with these studies is that the photophysical properties in fact experience a red shift (Fig. 2). The effect of the protonation is furthermore stronger on the fluorescence emission values, compared to the corresponding absorption values, which correlates with a more polar nature of the excited state,² again contradicting the anticipated results.

In general, the absorption maxima of the four chromophores experience a red shift of about $\Delta \lambda_{abs} = 10$ nm, while the red shifts for the emission range from $\Delta \lambda_{em} = 21$ nm for 6(+) to $\Delta \lambda_{em} = 64$ nm for 5(+) (Table 1). Analogous to the observations with their neutral congeners, 5(+) and 7(+)



Fig. 2 Normalized emission spectra of **5**, **7** (top), and **6**, **8** (bottom); neutral species: solid; protonated species: dashed; in CHCl₃.

show fairly similar emission profiles upon protonation $(\lambda_{em} \approx 580 \text{ nm})$, while 6(+) and 8(+) exhibit distinctly different profiles from each other. The polymer 8(+) shows the strongest red shift upon protonation with an emission at $\lambda_{em} = 624 \text{ nm}$ suggesting further extended conjugation within the scaffold. Notably, the emission maximum of 6(+) at $\lambda_{em} = 583 \text{ nm}$ is very similar to that of the other two molecular species 5(+) and 7(+). However, the further reduced photoluminescence quantum yields for the protonated species in the range of $\phi_{PL} < 0.09$ suggest the preservation of charge-transfer processes.

The necessity of a large amount of acid to trigger the halochromic response implies that the binding of protons to the chromophores is not very strong, suggesting the potential reversibility of the process. To investigate whether the acid



Fig. 3 Fluorescence for 5-8 changes upon treatment with TsOH.

response was indeed reversible, water was added to the CHCl₃ solutions of the protonated species to create a biphasic mixture. In our earlier studies we could show that water was a strong enough base to deprotonate the reported bis(dimethylaniline) species I by transferring the acid into the aqueous phase.⁷ A similar behavior was also observed for the chromophores **5–8** that all reverted back to their original emission colors upon treatment with water (Fig. 3). Remarkably, this process can be repeated several times without compromising the integrity of the chromophores.

The obtained data and observations strongly suggest that protonation does actually not occur at the nitrogen donor units. The only other possible option for the site of protonation is thus the phosphoryl group. It is well known that P==O bonds are strongly polar bonds and better described with the canonical structure P^+-O^- , which inherently creates the possibility for the oxide species to interact with electrophiles, such as protons, as confirmed by Pietschnig and co-workers for Me₃PO and HCl.¹² In fact, we have also recently reported the change in the photo-physics of acylated dithienophosphole oxides in the presence of Lewis acids, such as BF₃, that are based on similar interactions.¹³ Our studies could clearly show that the BF₃ coordinates to the P==O group rather than the C==O group that was also present in the molecules.

To lend the binding of protons to the P=O group in the present case more credibly, we have obtained ³¹P NMR spectroscopic data for the protonated versions of **6** and **7** that both show noticeably downfield-shifted resonances (**6**(+): $\Delta \delta = 2.1$ ppm; **7**(+): $\Delta \delta = 4.2$ ppm). The stronger shift for the D-A-D species can be explained with an increased polar (P⁺-O⁻) character in **7**(+) due to the effect of the two donor units that can transfer more electron density onto the cationic phosphorus center, thus stabilizing the polar (P⁺-O⁻) form, as opposed to the one donor in the A-D-A species **6**(+) that has to share its electron pair with two cationic phospholium centers.

To investigate the effect of the acid strength on the halochromism and to also confirm the generality of the acidchromophore interaction with the phosphoryl group, we then representatively treated **6** and **7** with trifluoroacetic acid (TFA). Again a large excess of acid is required, but a similar red shift of the emission is observed. However, due to the increased acidity of TFA compared to TsOH, the "protonated" versions of **6** and **7** show further red-shifted emission maxima at $\lambda_{\rm em} = 612$ nm and $\lambda_{\rm em} = 604$ nm, respectively (Fig. 4).



Fig. 4 Effects of different acids on the emission (normalized) of **6** (top) and **7** (bottom).

The different emission values obtained with the two acids as well as the necessity of large excess of acid are a strong indication that full protonation of the P==O group does not occur. Therefore, the halochromism of the four carbazole–dithienophosphole species is very likely the result of the formation of chromophore–acid complexes with $R_3P^+-O^- \rightarrow H\cdots A$ interactions.

Theoretical calculations

To gain a better understanding of the observed photophysics, and to further solidify the "protonation" at the phosphoryl group instead of the nitrogen centers, we have performed DFT calculations on two representative chromophores at the B3LYP/6-31G(d) level of theory that also include some representative examples of their N- and PO-protonated forms.¹⁴ For simplicity we have assumed full protonation of the PO group and truncated the dodecyl group with a N-methyl substituent. To counterbalance the effects of the absence of the corresponding anions, the calculations were performed using a PCM solvation model that has provided satisfactory results for cationic dithienophospholes in the past.^{6b,15} The energy values for the corresponding HOMO and LUMO levels are listed in Table 1. Fig. 5 shows the effects of N- and PO-protonation on the energy levels of **5**'.

The frontier orbitals for neutral 5' confirm that the HOMO is delocalized over the whole conjugated scaffold, while the LUMO is largely located at the dithienophosphole acceptor end of the chromophore, as expected. Protonation of the





Fig. 5 Frontier orbitals of **5**': (A) neutral species; (B) protonated at nitrogen; (C) protonated at PO.

nitrogen center has two major effects: (i) the energies of both HOMO and LUMO are lowered, but the energy gap between them remains fairly constant, and (ii) only one of the benzene rings in carbazole is part of the main conjugated scaffold, which consequently eliminates the possibility of N-protonation being responsible for the altered photophysics. Protonation of the phosphoryl group, on the other hand, results in a significantly lowered energy gap between HOMO and LUMO ($\Delta E = 0.87 \text{ eV}$), mostly due to a significantly lowered LUMO, supporting the red shift of the photophysics. From the frontier orbitals it is also clear that protonation of PO significantly increases the acceptor character of the dithienophosphole unit, as the HOMO is now largely located at the carbazole donor end, while the LUMO has less contribution from this unit compared to the neutral species.

To investigate the effects of the degree of protonation of the phosphoryl groups as well as to confirm the increased acceptor character of the protonated dithienophosphole *vs.* the neutral variety, we have also considered the mono- and di-PO-protonated 7' (A–D–A) for the calculations. Fig. 6 shows the effects of the stepwise protonation of the two PO-groups. In the neutral form, the HOMO is again evenly delocalized across the whole scaffold, while the LUMO is shifted toward both dithienophosphole acceptor units. Protonation of one PO-group results in a significant decrease in the energy gap from E = 3.22 eV (neutral) to E = 2.15 eV. Notably the HOMO now comprises of the carbazole and the non-protonated dithienophosphole, while the LUMO is exclusively located at the protonated acceptor character of the latter. Surprisingly, the second protonation

Fig. 6 Frontier orbitals of 7': (A) neutral species; (B) mono-PO protonated; (C) di-PO protonated.

results in an increase in the energy gap to E = 2.64 eV, which is mainly the result of a significantly lowered HOMO level that is somewhat shifted towards the carbazole unit. The LUMO and LUMO + 1 represent the two dithienophosphole acceptor groups, respectively.

The results from these calculations can also be used to explain the observed red-shifted emission maximum for the polymer **8**, compared to its D–A–D relative **6**. It is inherently plausible that the interaction of the molecular species **6** with TsOH leads to the interaction of both phosphoryl groups with the acid, while the morphology of the polymer **8** very likely does not allow for the complete interaction of all PO-groups with acid. The latter *de facto* creates mono-protonated triads (D–A–D⁺), with reduced energy gap, as supported by the theoretical calculations.

Conclusions

In conclusion, we have synthesized a series of donor/acceptor functionalized π -conjugated materials, in which the donor component is a 3(6)-carbazole unit and the acceptor component a 2(6)-dithienophosphole species. The carbazole was found to only have limited conjugation throughout its scaffold, and its effect on the photophysics is similar to that of an aniline substituent. The new chromophores show altered photophysics in the presence of large amounts of acids and the unexpected red-shifted absorption and emission maxima could be explained with the protonation of the P=O group of the dithienophosphole acceptor end, instead of the nitrogen-donor end

of the chromophores. The studies furthermore suggest that full protonation of the phosphoryl group does not occur, as the P=O is only a relatively weak nucleophile, but also that the process is reversible so that significantly different emission colors can be realized for the chromophores in the presence/ absence of acids. The latter clearly supports a desirable stimulus-responsive behaviour for this new kind of chromophore.

Experimental section

General

Reactions were carried out in dry glassware and under an inert atmosphere of purified nitrogen using Schlenk techniques. Solvents were dried using a MBraun solvent purification system. n-Butyllithium. 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxa-borolane, caesium fluoride, and tetrakis(triphenylphosphine)-palladium(0) were used as purchased from Sigma Aldrich or Oakwood, and liquids were distilled prior to use. 2-Bromodithieno-[3,2-b:2',3'-d]phosphole oxide $1,^9$ 2,6-dibromodithieno-[3,2-b:2',3'-d]phosphole oxide **2**, ^{5c} 3,6-dibromo-9-dodecyl-carbazole, and 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-dodecylcarbazole 3^{10} were prepared according to literature methods. ¹H NMR, ¹³C NMR, ³¹P NMR spectra were obtained on a Bruker UGI-400 or RDQ-400 spectrometer. Chemical shifts are reported in ppm, referenced to external 85% H_3PO_4 (³¹P) or solvent signal (¹H, ¹³C); ¹³C NMR was measured with proton decoupling and the attached proton test (APT); ³¹P NMR spectra were measured with proton decoupling. Elemental analyses were performed in the Department of Chemistry at the University of Calgary. MALDI-TOF mass spectra were run on a Bruker Daltonics AutoFlex III system. Photophysical data were obtained from chloroform solutions using a Jasco FP-6600 spectrometer and an UV-Vis-NIR Cary 5000 spectrometer. Gel permeation chromatography (GPC) analyses were carried out on a Waters Breeze instrument in THF solutions. Molecular weights are reported against polystyrene standards.

Syntheses

3,6-Bis(4,4,5,5,-tetramethyl-1,3,2-dioxaborolan)-9-dodecyl-carbazole 4. 3,6-Dibromo-9-dodecyl-carbazole (3.541 g, 7.168 mmol) was dissolved in THF (50 mL) and was added dropwise to a solution of n-BuLi (6.6 mL, 15.77 mmol, 2.5 M in hexanes) in THF (10 mL) at -78 °C with stirring. The mixture was left to stir for 2 h, following the addition of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dixoaborolane (2.992 g, 16.09 mmol) dropwise at -78 °C and then left to stir overnight to reach room temperature. Upon reaction, water (25 mL) was added to the solution and stirred for an additional 30 min, resulting in a pale brown solution. This mixture was extracted with ether and the organic layer was washed with water, dried over MgSO4 and solvent was evaporated under reduced pressure. The clear yellow oil was purified by column chromatography on silica using hexanes and ethyl acetate. Purified 4 (652 mg, 15%) was obtained as a colorless oil. ¹H NMR (400 MHz; CDCl₃) 0.88 (3H, t, ${}^{3}J_{H,H} = 6.8$ Hz, CH₃), 1.24–1.33 (18H, br m, CH₂), 1.40 (24H, s, pin-CH₃), 1.83-1.90 (2H, m, CH₂), 4.32 (2H, t, ${}^{3}J_{H,H} = 7.2$ Hz, α -CH₂), 7.40 (2H, dd, ${}^{5}J_{H,H} = 0.8$ Hz, ${}^{3}J_{H,H}$ = 8.4 Hz, Ar), 7.92 (2H, dd, ${}^{4}J_{H,H}$ = 1.2 Hz,

³*J*_{*H*,*H*} = 8.4 Hz, Ar), 8.68 (2H, dd, ⁵*J*_{*H*,*H*} = 0.8 Hz, ⁴*J*_{*H*,*H*} = 1.2 Hz, Ar); ¹³C{¹H} NMR (100 MHz, CDCl₃) 14.4 (s, CH₃), 22.8 (s, CH₂), 25.0 (s, CH₂), 27.3 (s, CH₂), 29.0 (s, CH₂), 29.4 (s, CH₂), 29.5 (s, CH₂), 29.5 (s, CH₂), 29.6 (s, CH₂), 29.7 (s, CH₂), 29.8 (s, CH₂), 32.0 (s, CH₂), 43.2 (s, α-CH₂), 83.5 (s, O–C), 108.2 (s, Ar), 118.9 (s, B–Ar), 122.9 (s, Ar), 128.1 (s, Ar), 132.1 (s, Ar), 142.7 (s, Ar).

Compound 5 (A–D). 2-Bromodithieno[3,2-b:2',3'-d]phosphole oxide (64 mg, 0.17 mmol), 3-(4,4,5,5-tetramethyl-1,3,2dioxaborolan-2-vl)-9-dodecylcarbazole (318 mg, 0.69 mmol), caesium fluoride (205 mg, 1.36 mmol), and [Pd(PPh₃)₄] (45 mg, 0.03 mmol) were dissolved in THF (20 mL) and refluxed at 70 °C for 72 h. After cooling, the mixture was extracted with chloroform. The organic phase was washed with saturated NH₄Cl solution and water, dried over MgSO₄ and solvent was evaporated under reduced pressure to give a brown oil. Compound 5 (35 mg, 33%) was isolated by column chromatography on silica using chloroform and ethyl acetate (1:1) as a yellow solid; ¹H NMR (400 MHz; CDCl₃) 0.88 (3H, t, ${}^{3}J_{HH} =$ 6.6 Hz, CH₃), 1.24-1.38 (18H, br m, CH₂), 1.84-1.91 (2H, m, CH₂), 4.29 (2H, t, ${}^{3}J_{H,H} = 7.2$ Hz, α -CH₂), 7.11 (1H, dd, ${}^{4}J_{H,P} = 2.4$ Hz, ${}^{3}J_{H,H} = 4.8$ Hz, S₂PO), 7.19 (1H, td, ${}^{4}J_{H,H} =$ 0.8 Hz, ${}^{3}J_{H,H} = 7.6$ Hz, cbz), 7.23 (1H, dd, ${}^{4}J_{H,P} = 3.6$ Hz, ${}^{3}J_{HH} = 5.2$ Hz, S₂PO), 7.31 (1H, d, ${}^{4}J_{HP} = 2.8$ Hz, S₂PO), 7.34 (2H, t, ${}^{3}J_{H,H} = 8.0$ Hz, cbz), 7.37–7.42 (3H, m, *m*-Ph (2H) and cbz (1H)), 7.47–7.51 (1H, m, *p*-Ph), 7.57 (1H, dd, ${}^{3}J_{H,H} =$ 8.4 Hz, ${}^{4}J_{H,H} = 2.0$ Hz, cbz), 7.74–7.90 (2H, m, o-Ph), 8.03 (1H, d, ${}^{3}J_{H,H} = 7.6$ Hz, cbz), 8.19 (1H, d, ${}^{4}J_{H,H} = 2.0$ Hz, cbz); ${}^{31}P{}^{1}H$ NMR (121.5 MHz, CDCl₃) 20.04; ${}^{13}C{}^{1}H$ NMR (100 MHz, CDCl₃) 14.2 (s, CH₃), 22.7 (s, CH₂), 27.3 (s, CH₂), 29.0 (s, CH₂), 29.3 (s, CH₂), 29.4 (s, CH₂), 29.5 (s, CH₂), 29.6 (s, CH₂), 29.6 (s, CH₂), 31.9 (s, CH₂), 43.3 (s, α-CH₂), 109.1 (s, cbz), 109.3 (s, cbz), 117.8 (s, cbz), 119.3 (s, cbz), 120.2 (d, $J_{C,P} = 14.3$ Hz, Ar), 120.5 (s, cbz), 122.6 (s, cbz), 123.3 (s, cbz), 123.9 (s, cbz), 124.6 (s, cbz), 126.0 (d, $J_{CP} = 14.3$ Hz, Ar), 126.3 (s, cbz), 127.9 (d, $J_{CP} = 14.9$ Hz, Ar), 128.9 (d, $J_{C,P} = 13.0$ Hz, Ar), 129.9 (d, ${}^{1}J_{C,P} = 107.1$ Hz, *ipso*-Ph), 131.0 (d, $J_{C,P} = 11.3$ Hz, Ar), 132.4 (d, $J_{C,P} = 2.6$ Hz, *p*-Ph), 138.5 (d, ${}^{1}J_{C,P}$ = 112.1 Hz, *ipso*-Ar), 139.8 (d, ${}^{1}J_{C,P} = 109.4$ Hz, *ipso*-Ar), 140.4 (s, cbz), 141.0 (s, cbz), 142.9 (d, $J_{CP} = 22.9$ Hz, Ar), 146.6 (d, $J_{CP} = 24.6$ Hz, Ar), 150.2 (d, $J_{C,P} = 14.5$ Hz, Ar); HR-MALDI/TOF-MS: m/z 621.2283 (M⁺. C₆₂H₇₁N₂OPS₂ requires 621.2289).

Compound 6 (D–A–D). 2,6-Dibromodithieno[3,2-*b*:2',3'-*d*]phosphole oxide (220 mg, 0.49 mmol), 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-dodecylcarbazole (721 mg, 1.56 mmol), caesium fluoride (558 mg, 3.70 mmol), and [Pd(PPh₃)₄] (60 mg, 0.04 mmol) were dissolved in THF (25 mL) and refluxed for 70 °C for 72 h. After cooling, the mixture was extracted with chloroform. The organic phase was washed with saturated NH₄Cl solution and water, dried over MgSO₄ and solvent was evaporated under reduced pressure to afford a dark brown solid. Compound **6** (60 mg, 13%) was isolated by column chromatography on silica using chloroform and ethyl acetate (1 : 1) as a red solid (found: C, 77.01; H, 7.41; N, 2.74. C₆₂H₇₁N₂OPS₂ requires C, 77.95; H, 7.49; N, 2.93%); ¹H NMR (400 MHz; CDCl₃) 0.90 (6H, t, ³J_{H,H} = 7.0 Hz, CH₃), 1.26–1.38 (36H, br m, CH₂), 1.86–1.93 (4H, m, CH₂), 4.31 (4H, t, ${}^{3}J_{H,H} = 7.2$ Hz, α -CH₂), 7.29 (2H, td, ${}^{4}J_{H,H} = 0.8$ Hz, ${}^{3}J_{H,H} = 7.4$ Hz, cbz), 7.40–7.44 (6H, m, cbz (4H) and S2PO (2H)), 7.48-7.54 (4H, m, m-Ph (2H) and cbz (2H)), 7.56-7.61 (1H, m, p-Ph), 7.90-7.96 (2H, m, o-Ph), 8.13 (2H, d, ${}^{3}J_{H,H} = 7.6$ Hz, cbz), 8.28 (2H, d, ${}^{4}J_{H,H} = 1.6$ Hz, cbz); ${}^{31}P{}^{1}H{}$ NMR (121.5 MHz, CDCl₃) 21.24; ¹³C{¹H} NMR (100 MHz, CDCl₃) 14.2 (s, CH₃), 22.7 (s, CH₂), 27.3 (s, CH₂), 29.0 (s, CH₂), 29.4 (s, CH₂), 29.4 (s, CH₂), 29.5 (s, CH₂), 29.6 (s, CH₂), 29.6 (s, CH₂), 31.9 (s, CH₂), 43.3 (s, α-CH₂), 109.0 (s, cbz), 109.2 (s, cbz), 117.7 (s, cbz), 119.3 (s, cbz), 120.2 (d, $J_{C,P} = 14.4$ Hz, Ar), 120.6 (s, cbz), 122.6 (s, cbz), 123.4 (s, cbz), 123.9 (s, cbz), 124.6 (s, cbz), 126.2 (s, cbz), 129.0 (d, $J_{C,P} = 13.0$ Hz, Ar), 130.2 (d, ${}^{1}J_{C,P} = 106.6$ Hz, *ipso*-Ph), 131.1 (d, $J_{C,P} = 11.4$ Hz, Ar), 132.4 (d, $J_{C,P} = 2.8$ Hz, p-Ph), 138.7 (d, ${}^{1}J_{C,P} = 111.4$ Hz, *ipso*-Ar), 140.4 (s, cbz), 141.0 (s, cbz), 143.6 (d, $J_{CP} = 23.3$ Hz, Ar), 149.7 (d, $J_{C,P} = 14.6$ Hz, Ar); HR-MALDI/TOF-MS: m/z 954.4707 (M⁺. C₆₂H₇₁N₂OPS₂ requires 954.4745).

Compound 7 (A–D–A). 2-Bromodithieno[3,2-b:2',3'-d]phosphole oxide (367 mg, 1.00 mmol), 3,6-bis(4,4,5,5,-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-dodecylcarbazole (245 mg, 0.42 mmol), caesium fluoride (434 mg, 2.86 mmol) and [Pd(PPh₃)₄] (45 mg, 0.03 mmol) were dissolved in THF (30 mL) and heated to 65 °C for 72 h. After cooling, water was added and the mixture was extracted with chloroform. The organic phase was washed with saturated NH₄Cl solution and water, dried over MgSO4 and solvent was evaporated under reduced pressure to give a dark orange oil. Pure 7 (141 mg, 37%) was isolated by column chromatography on silica using ethyl acetate and acetone (1:0 to 0:1) as a golden yellow solid (found: C, 67.61; H, 5.29; N, 1.54. C₅₂H₄₇NO₂P₂S₄ requires C, 68.77; H, 5.22; N, 1.54%); ¹H NMR (400 MHz; CDCl₃) 0.89 (3H, t, ${}^{3}J_{H,H} = 7.0$ Hz, CH₃), 1.25 (18H, br m, CH₂), 1.85–1.92 (2H, m, CH₂), 4.31 (2H, t, ${}^{3}J_{H,H} = 7.0$ Hz, α -CH₂), 7.20 (2H, dd, ${}^{4}J_{H,P} = 2.4$ Hz, ${}^{3}J_{H,H} = 4.8$ Hz, 6,6'-H, S₂PO), 7.31 (2H, dd, ${}^{3}J_{H,P} = 3.4$ Hz, ${}^{3}J_{H,H} = 4.8$ Hz, 5,5'-H, S_2PO), 7.39 (2H, d, ${}^4J_{H,P}$ = 2.4 Hz, 3,3'-H, S_2PO), 7.41 (2H, d, ${}^{4}J_{H,H} = 8.4$ Hz, cbz), 7.46–7.50 (4H, m, *m*-Ph), 7.56–7.60 (2H, m, *p*-Ph), 7.68 (2H, dd, ${}^{3}J_{H,H} = 8.4$ Hz, ${}^{4}J_{H,H} = 1.6$ Hz, cbz), 7.81–7.87 (4H, m, *o*-Ph), 8.27 (2H, d, ${}^{4}J_{H,H} = 1.6$ Hz, cbz); ³¹P{¹H} NMR (121.5 MHz, CDCl₃) 20.64; ¹³C{¹H} NMR (100 MHz, CDCl₃) 14.1 (s, CH₃), 22.7 (s, CH₂), 27.3 (s, CH₂), 29.0 (s, CH₂), 29.3 (s, CH₂), 29.4 (s, CH₂), 29.5 (s, CH₂), 29.5 (s, CH₂), 31.9 (s, CH₂), 43.5 (s, α-CH₂), 109.7 (s, cbz), 118.0 (s, cbz), 120.4 (d, $J_{C,P} = 14.6$ Hz, Ar), 123.2 (s, cbz), 124.5 (s, cbz), 125.1 (s, cbz), 126.9 (d, $J_{C,P} = 14.5$ Hz, Ar), 128.5 (d, $J_{C,P} = 14.8$ Hz, Ph), 129.9 (d, ${}^{1}J_{C,P} = 107.1$ Hz, *ipso*-Ph), 131.5 (d, $J_{C,P} = 11.1$ Hz, Ar), 132.5 (d, $J_{C,P} = 2.6$ Hz, p-Ph), 137.8 $(d, {}^{1}J_{C,P} = 112.3 \text{ Hz}, ipso-Ar), 140.0 (d, {}^{1}J_{C,P} = 110.6 \text{ Hz}, ipso-Ar),$ 140.9 (s, cbz), 143.1 (d, $J_{C,P}$ = 22.9 Hz, Ar), 146.5 (d, $J_{C,P}$ = 21.4 Hz, Ar), 149.8 (d, $J_{C,P} = 14.0$ Hz, Ar); HR-MALDI/ TOF-MS: m/z 907.1957 (M⁺. C₅₂H₄₇NO₂P₂S₄ requires 907.1965).

Polymer 8. 2,6-Dibromodithieno[3,2-b:2',3'-d]phosphole oxide (232 mg, 0.52 mmol), 3,6-bis(4,4,5,5,-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-dodecylcarbazole (306 mg, 0.52 mmol), caesium fluoride (570 mg, 3.77 mmol), and [Pd(PPh_3)_4]

(0.60 mg, 0.04 mmol) were dissolved in THF (20 mL), degassed, and heated to 65 °C for 72 h. After cooling, the solution was precipitated in methanol (1 L) and the precipitated polymer was collected on a Buchner funnel. The precipitated solids were washed with hot methanol, hexanes, and then taken up in chloroform. The solution was evaporated to dryness under reduced pressure to afford polymer 8 (40 mg, 8%) as a dark orange film; ¹H NMR (400 MHz; CDCl₃) 0.88-0.90 (br m, CH₃), 1.25-1.28 (br m, CH₂), 1.80-1.87 (br m, CH₂), 4.29-4.32 (br m, α-CH₂), 7.50-7.54 (br m, S₂PO), 7.55-7.59 (br m, Ph), 7.66-7.75 (br m, Ph), 7.81-7.86 (br m, cbz), 7.92-7.97 (br m, Ph), 8.23-8.28 (br m, cbz), 8.64 (br s, cbz); ${}^{31}P{}^{1}H{}$ NMR (121.5 MHz, CDCl₃) 21.34 (br s); $^{13}C{^{1}H}$ NMR (100 MHz, CDCl₃) 14.1 (br s, CH₃), 22.7 (br s, CH₂), 27.3 (br s, CH₂), 29.0 (br s, CH₂), 29.3 (br s, CH₂), 29.4 (br s, CH₂), 29.5 (br s, CH₂), 29.5 (br s, CH₂), 31.9 (br s, CH₂), 43.3 (br s, α-CH₂), 109.3 (br s, cbz), 109.6 (br s, cbz), 117.9 (br s, cbz), 120.2 (br s, cbz), 120.3 (br s, Ar), 120.5 (br s, cbz), 122.4 (br s, cbz), 123.2 (br s, cbz), 123.7 (br s, cbz), 124.4 (br s, cbz), 125.1 (br d, $J_{CP} = 12.8$ Hz, Ar), 125.2 (br s, cbz), 128.5 (br d, $J_{C,P} = 14.5$ Hz, Ar), 129.0 (br d, $J_{C,P} = 14.0$ Hz, Ar), 130.9 (d, ${}^{1}J_{C,P} = 113.9$ Hz, *ipso*-Ph), 131.9 (br d, $J_{C,P} =$ 3.3 Hz, p-Ph), 132.6 (br d, $J_{C,P} = 12.0$ Hz, Ar), 137.8 (br d, ${}^{1}J_{C,P} = 107.4$ Hz, *ipso*-Ar), 138.7 (br d, ${}^{1}J_{C,P} = 111.3$ Hz, *ipso*-Ar), 140.5 (s, cbz), 140.8 (s, cbz), 143.1 (br d, $J_{C,P} = 20.3$ Hz, Ar), 146.6 (br s, Ar), 149.7 (br s, Ar); GPC analysis (THF solution): $M_{\rm w} = 2568 \text{ g mol}^{-1}$; $M_{\rm n} = 1486 \text{ g mol}^{-1}$; PDI = 1.7.

Acknowledgements

Financial support by NSERC of Canada and the Canada Foundation for Innovation (CFI) is gratefully acknowledged. M. S. thanks the University of Calgary for a PURE scholarship.

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