Dendrimeric Oligo(phenylenevinylene)-Extended Dithieno[3,2-b:2',3'd]phospholes—Synthesis, Self-Organization, and Optical Properties

Carlos Romero-Nieto,^[a, b] Sonia Merino,^[b] Julián Rodríguez-López,^{*[b]} and Thomas Baumgartner^{*[a]}

Dedicated to Edgar Niecke on the occasion of his 70th birthday.

Abstract: To establish this system as a fluorescent core in π -conjugated dendrimers, a series of oligo(phenylenevinylene) (OPV)-extended dithieno[3,2-b:2',3'-d]phospholes has been prepared by means of a Wittig–Horner protocol with a dithienophosphole dialdehyde and appropriately functionalized phosphonates. The "zero-generation" model compounds have provided the general accessibility of OPV-functionalized dithienophospholes, and show varying

Introduction

Organic π -conjugated materials are known for their beneficial photophysical and electronic properties that provide intriguing opportunities for the field of organic electronics. Their (semi)conducting properties show great potential for application in organic electronic devices such as molecularor polymer-based light-emitting diodes, photovoltaic cells, field-effect transistors, or sensory materials, to name but a few.^[1-7] To date, a large variety of material classes, encom-

[a]	C. Romero-Nieto, Prof. Dr. T. Baumgartner Department of Chemistry, University of Calgary 2500 University Drive NW, Calgary AB T2N 1N4 (Canada)
	Fax: (+1)403-289-9488 E-mail: Thomas.baumgartner@ucalgary.ca
[b]	C. Romero-Nieto, Prof. Dr. S. Merino, Prof. Dr. J. Rodríguez-López Facultad de Química Universidad de Castilla-La Mancha 13071 Ciudad Real (Spain) Fax: (+34)926295318 E-mail: julian.rodriguez@uclm.es

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200802482.

emission colors covering the optical spectrum from green to red. Expansion of the synthetic strategy towards the corresponding first-generation dendrimers has provided materials that show intriguing self-organization fea-

Keywords: conjugation • dendrimers • density functional calculations • organic electronics • phosphorus heterocycles

tures in case of the phenyl-terminated dendrimer, forming large one-dimensional microfibres, as well as desirable energy-transfer processes from the dendrons to the dithienophoshole core resulting in an enhanced emission intensity for the latter. The present study has revealed that the terminal endgroups of the OPV branches have significant impact on the optical features of the OPV dendrimers as a whole.

passing small molecules, oligomers, and polymers, have not only proven to be quite successful in these applications, but have also underscored the structural flexibility of organic electronics in general. Among the larger assemblies, π -conjugated, shape-persistent dendrimers have evolved as a promising class of materials in recent years, as they provide both new methodologies and molecular architectures that allow the controlled synthesis of large "super-molecules" with well-defined microstructures and electronics.^[8] Dendrimers that are based on phenylenevinylene building blocks, with meta arrangement of stilbene units in the branches, are particularly interesting in this context.^[9] Their specific geometry furnishes them with photophysical properties that are quite beneficial for light-emitting applications.^[10] In particular, the branches can act as light-harvesting antennae that behave as an ensemble of almost independent chromophores relaying incoming photons to the emissive, central core. As a result of this energy transfer (ET), the core then shows enhanced emission intensity.

In the context of organic electronics, the incorporation of phosphorus centers into π -conjugated materials has also recently drawn an increasing amount of attention.^[11] The versatile reactivity and electronic nature of phosphorus offer considerable opportunities for the development of new ma-

Chem. Eur. J. 2009, 15, 4135-4145

© 2009 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



terials with intriguing properties.^[11b] Trivalent phosphorus species, in general, can react with oxidizing agents or Lewis acids, and they can also coordinate to transition metals, offering a unique variety of synthetically facile possibilities to efficiently modify the electronic properties of the product materials.^[11b,12] Phosphole-containing materials are of particular interest, due to the pyramidal structure of the tricoordinate phosphorus center, which limits an efficient orbital interaction of the phosphorus lone-pair with the conjugated system. In addition, the phosphole system exhibits a peculiar electronic structure, with a low-lying LUMO energy level that is particularly attractive for organic electronics.^[13] Réau and co-workers were among the first to incorporate the phosphole moiety in extended π -conjugated materials^[14] and to utilize these in phosphole-based OLED devices.^[15] A few years ago, we introduced the dithieno [3,2-b:2',3'-d] phosphole system (1, Scheme 1) to this field of research.^[16] Our



Scheme 1. Synthesis of the diformylated dithienophosphole 2: a) 2 LDA, THF, -78 °C; b) DMF (excess), -78 °C.

building block, which conjoins two thiophene subunits with a central phosphole moiety through annelation, allows for the selective and efficient tuning of the (opto)electronic properties of the materials by functionalization of phosphorus atom or the main scaffold.^[16,17] The materials obtained in the context of our studies, display highly advantageous, unprecedented photophysical properties with respect to emission wavelengths, intensity, and tunability. Since then, the groups of Yamaguchi^[18] and Matano,^[19] among others, were able to further solidify the benefits of phosphole units within π -conjugated assemblies, reporting materials with remarkable optoelectronic properties. In 2007, Sanji, Shiraishi, and Tanaka reported the first phosphole-cored dendrimers with enhanced emission intensities resulting from an energytransfer (ET) from the branches to the core.^[20]

In this paper we now report a new functionalization of the dithienophosphole system and its subsequent incorporation into extended, π -conjugated dendrimers with donor or acceptor end-groups. This study was performed with the intention to incorporate the dithienophosphole unit as a fluorescent core in dendrimeric structures and further enhance the powerful photophysical properties of this system through light-harvesting dendrons with *m*-phenylenevinylene linkages.

Results and Discussion

Evaluation of the synthetic strategy with model compounds: One of the general synthetic strategies toward oligo(phenylenevinylene) (OPV) systems involves Wittig–Horner coupling reactions between aldehydes and phosphonates.^[9] Conveniently, this synthetic strategy provides for a selective formation of *E*-configured vinylene bridges,^[10] which are beneficial for the spatial placement of the dendritic segments and ultimately for the dendrimer as a whole. For this reason, we looked into the functionalization of the dithienophosphole scaffold with formyl groups in the 2- and 6-positions of **1** (Scheme 1). Formylation can be achieved in good yields (89%) by reaction of the 2,6-dilithiated dithienophosphole, obtained according to a procedure published by us earlier using lithium diisopropyl amide (LDA),^[17a] with a large excess DMF at low temperatures.

Compound **2** has a ³¹P NMR resonance at $\delta = -19.8$ ppm that is only slightly low-field shifted with respect to that of the parent system **1** (cf. -21.5 ppm),^[16a] supporting the preservation of trivalent phosphorus center during the reaction; ¹H and ¹³C NMR data are consistent with this assumption. The fluorescence data of **2** exhibit red-shifted values for excitation ($\lambda_{ex} = 391$ nm) and emission ($\lambda_{em} = 457$ nm) that are consistent with an extended delocalization of the π -system throughout the formyl groups (see Table 1). Notably, the

Table 1. Fluorescence spectroscopy data for 1, 2 and 4a-d.

	$\lambda_{\mathrm{ex}} \; [\mathrm{nm}]^{[\mathrm{a}]}$	$\lambda_{em} [nm]^{[b]}$	$\phi_{ ext{PL}}$
1 ^[11a]	338	415	0.78 ^[d]
2	391	457	0.03 ^[d]
4a	401, 487	507	0.37 ^[c]
4b	452, 484 (sh)	516	0.35 ^[c]
4c	386, 498	526	0.35 ^[c]
4d	415, 521	631	0.25 ^[c]

[a] λ_{max} for excitation. [b] λ_{max} for emission. [c] Relative to fluorescein (in 0.01 M KOH/ethanol); $\pm 15\%$; in CH₂Cl₂. [d] Relative to quinine sulfate (0.1 M H₂SO₄ solution); $\pm 15\%$; in CH₂Cl₂.

quantum yield of 2 experiences a dramatic drop down to $\phi_{\rm PL} = 0.03$ (from $\phi_{\rm PL} = 0.78$ in **1**) indicating significant quenching caused by the formyl groups. We were also able to obtain suitable single crystals of 2 for an X-ray diffraction study from a concentrated CH₂Cl₂/hexanes (1:1) solvent mixture at room temperature.^[21] The structure and packing of 2 in the solid state are shown in Figure 1. The bond lengths and angles of the diformylated compound 2 are related to those of the parent dithienophosphole $\mathbf{1}^{[16a]}$ and show good π -delocalization, as well as a doping effect of the phosphorus center. Some slightly different metric parameters can be attributed to the electronic effect of the formyl groups. However, it is interesting to note that the formyl groups lie in the same plane as the π -conjugated scaffold (torsion angles $<6^{\circ}$) with the oxygen atoms oriented towards the thiophene sulfur atoms. This orientation can be explained by intermolecular interactions in the solid state, for which a significant degree of π -stacking can be observed between neighboring molecules (distance 3.457 Å; Figure 1 inset).



Figure 1. Molecular structure (50% probability level) and packing (inset) of **2** in the solid state. Selected bond lengths [Å] and angles [°]: P1–C4 1.8280(19), P1–C7 1.8270(18), P1–C11 1.8436(18), C1–O1 1.215(2), C1–C2 1.454(3), C10–O2 1.209(2), C9–C10 1.451(3), C4–C5 1.388(2), C5–C6 1.444(2), C6–C7 1.388(2); C4-P1-C11 98.22(8), C4-P1-C7 88.43(8), C7-P1-C11 102.02(8); torsion O1-C1-C2-S1 5.41, O2-C10-C9-S2 1.17.

With the diformylated dithienophosphole 2 in hand, the feasibility and scope of accessing extended π -systems with vinylene bridges by means of a Wittig-Horner protocol was tested. The model studies involved the formation of a series of "zero"-generation dendrimers, that is, phenyl-terminated groups that were furnished with donor or acceptor groups in the para-position. We were interested in how-if at allthese peripheral groups would affect the optoelectronic properties of the respective materials. The dialdehyde building block 2 was treated with an appropriate set of p-functionalized benzyl phosphonates 3a-d (R-C₆H₄-CH₂-P(O)- $(OEt)_2$; **a**: R = H; **b**: OMe; **c**: CF₃; **d**: NPh₂) to form the corresponding vinylene-bridged, extended materials in the presence of tBuOK as base (Scheme 2). It should be mentioned in this context that Wittig-Horner reactions with thienyl aldehydes have been found to be problematic in the past; a deformylation byproduct is often formed.^[22] To avoid this undesired side reaction, we have devised a synthetic protocol, using native benzyl diethylphosphonate as reagent, by which we were able to successfully generate an extended structure 4a without any deformylation byproducts. With the modified protocol (see experimental section), the donorand acceptor-functionalized species 4b and 4c, respectively, could also be successfully synthesized. It should be noted that the reaction towards 4c occurs even more readily than with the native phenyl species, likely through the effect of the p-CF₃ group that activates the benzylic position for deprotonation during the Wittig-Horner reaction stabilizing the resulting anionic charge.

It is worth noting that under the same conditions the reaction with the electron-rich, NPh_2 -functionalized benzyl phosphonate was found to be quite sluggish. The explanation for this behavior, again, lies in the tendency for deprotonation of the benzylic position, which now is deactivated by the *p*-



FULL PAPER

Scheme 2. Synthesis of extended phenylenevinylene dithienophospholes: a) 2.3 R-C₆H₄-CH₂-P(O)(OEt)₂, 2.2 *t*BuOK, THF, -78 °C, 1 h (**4a**: R = H, **4b**: R = OMe, **4c**: R = CF₃); b) 2.3 Ph₂N-C₆H₄-CH₂-P(O)(OEt)₂, 2.2 *t*BuOK, THF, -78 °C, 4 h (**4d**: R = NPh₂); c) H₂O₂ (excess), CH₂Cl₂, RT (R = H).

NPh₂ group. However, a prolonged reaction time (4 h) was found to drive this reaction towards the desired difunctionalized species 4d. All extended materials 4a-d exhibit ³¹P magnetic resonances around $\delta = -20.0(\pm 0.2)$ ppm that are almost identical with that of the dialdehyde 2. The ¹H and ¹³C NMR data are also closely related to those of **2**. The ${}^{3}J(H,H)$ coupling constants of 16.0(±0.1) Hz for the vinylic protons clearly support the selective formation of E-configured double bonds.^[9,10] It should be emphasized that this synthetic protocol also preserves the trivalent phosphorus center of the dithienophosphole core. This very beneficial feature allows the utilization of the versatile reactivity of this center immediately after the coupling to further finetune the electronic properties in subsequent reactions, without any deprotection steps.^[17b] Investigation of the optoelectronic properties of the extended materials 4a-d by means of fluorescence spectroscopy showed that the π -conjugated system can be effectively expanded by this method, generating compounds with fluorescence emission colors that depend on the functional group at the terminal periphery, ranging from green to red (see Table 1). Notably, compared to dialdehyde 2, their quantum yields are significantly improved ($\phi_{PL} = 0.24 - 0.37$), but they are still lower than in the parent phosphole 1 (cf. $\phi_{PL}=0.78$), likely due to additional degrees of freedom present in the extended materials. Importantly, compound 4d shows the most red-shifted emission value of a dithienophosphole-based molecular material to date at $\lambda_{em} = 631$ nm. Compared to a diphenylaniline-extended dithienophosphole ($\lambda_{em} = 566 \text{ nm}$) reported by us earlier,^[17b] the presence of the two additional double bonds in **4d** accounts for a red-shift of an additional 65 nm. Notably, the emission value of **4d** is only 27 nm less red-shifted from the value of a dithienophosphole-containing polymer ($\lambda_{em} = 658$ nm) reported by us recently,^[23] which suggests a potential application of **4d** as molecular dye in organic photovoltaic cells.

To improve the acceptor properties of the central phosphorus atom,^[16,17] as well as to obtain a suitable photophysical reference material for the targeted dendrimers (vide infra), we oxidized the phosphorus atom of the phenylvinylene extended compound 4a in our typical protocol using hydrogen peroxide in dichloromethane at room temperature.^[16] Complete conversion of the trivalent phosphorus center to the phosphole oxide can be monitored by ³¹P NMR spectroscopy, showing a distinct lowfield shift for the product 5 at $\delta = 18.6$ ppm that is typical for these compounds; ¹H and ¹³C NMR spectra also show consistent data. Another indication of the successful transformation of 5 is the fluorescence emission at $\lambda_{em} = 551$ nm that is red-shifted by about $\Delta \lambda_{\rm em} = 44$ nm from that of the non-oxidized starting material; oxidation of the phosphorus center in dithienophospholes in general affords a red-shift of 40-50 nm due to a lowered LUMO level.^[16,17]

Synthesis and properties of dendrimeric dithienophospholes:

Having verified the general accessibility of phenylenevinylene-extended dithienophospholes through the "zerogeneration" model compounds, corresponding "first-generation" materials were synthesized in a similar Wittig–Horner protocol. Appropriate benzyl phosphonates **8a–c** were obtained in a modified procedure from the one reported by Marder et al.,^[22a] using benzylic alcohols **7a–c** (accessible from the corresponding carboxylic acids **6a–c**^[24] by reduction with LiAlH₄, Scheme 3), instead of the generally applied benzyl halides.^[25] It should be mentioned in this con-



Scheme 3. Synthesis of the dendronized dithienophosphole oxides 9a-c.

The three benzyl phosphonates **8a–c** were then treated with the dithienophosphole dialdehyde **2** in a similar procedure as used for the zero-generation model compounds, followed by in situ oxidation of the phosphorus center with hydrogen peroxide to provide the dendronized materials **9a–c** in decent isolated yields (**9a**: 53%; **9b**: 43%; **9c**: 49%).

The oxidation of the phosphorus center was performed to provide air- and moisture-stable materials, but more importantly, to also enhance the acceptor character of the dithienophosphole core for an optimized energy transfer from the branches. ³¹P NMR shifts of $\delta = 19.8$ (9a), 13.4 (9b), and 18.3 ppm (9c) indicate the successful oxidation of the phosphorus centers, as they are in the typical range for oxidized dithienophospholes (cf.: $\delta = 17.0(\pm 3)$ ppm), and also relate to the model compound **5** ($\delta = 18.6$ ppm).^[16,17] The different shifts observed furthermore reflect the electronic impact of the terminal end-groups on the conjugated system. ¹H NMR data also support the formation of the desired dendrimers **9a-c** with *trans*-configured stilbene units $({}^{3}J(H,H) =$ 16.0 Hz). All three compounds exhibit significant thermal stability, as determined by differential scanning calorimetry (DSC), showing decomposition only above 320°C (9a: $T_{\text{decomp}} = 379.8 \,^{\circ}\text{C}; \quad \mathbf{9b}: \quad T_{\text{decomp}} = 384.3 \,^{\circ}\text{C}; \quad \mathbf{9c}: \quad T_{\text{decomp}} =$ 323.0 °C), with melting points just below at $T_{\rm m} = 340.8$ °C (9a) and $T_m = 379.2$ °C (9b); 9c decomposes without prior melting process.

Likely due to the polar nature of their terminal endgroups, dendrimers **9b** and **9c** show satisfying solubility in a variety of organic solvents, such as THF, chloroform, dichloromethane, and tetrachloroethane, whereas the "unsubstituted" dendrimer 9a is only somewhat soluble in THF and tetrachloroethane. This fact can be explained by the large, shape-persistent, planar π -system in **9a** that allows for extended π -stacking interactions between neighboring molecules. As a matter of fact, dendrimer 9a self-organizes in THF into large one-dimensional (1D) microfibres of random length up to about 250 µm, but fairly consistent narrow width (1.6-1.9 µm), as observed by deconvolution fluorescence microscopy (Figure 2). It should be mentioned that most nano-structured 1D morphologies to date are based on inorganic materials, whereas the number of organic 1D morphologies is fairly limited. The self-organized 1D microfibres of 9a are thus rather intriguing, as they might prove useful for application in organic devices for which high-order is required for superior charge-transport phenomena (e.g., in organic field-effect transistors), in combination with the flexibility provided by the organic nature of the materials.^[26] A similar self-organization process is not observed for 9b or 9c, probably due to the bulky nature of

4138



Figure 2. Confocal fluorescence micrographs of the self-organized 1Dfibres of 9a in THF at different magnification rates, as indicated at the bottom left corners of the figures (µm-scale).

the terminal end-groups that limit extended π -stacking interactions.

It should be noted in this context that the 1D microfibres of **9a** are only stable in the presence of THF. Evaporation of the solvent leads to a degeneration of the fibres and results in the formation of an amorphous powder. This observation indicates that the THF is very likely part of the selforganization process, as well as the 1D-organizational structure as a whole, which is a known feature for OPV systems.^[27] Although the supramolecular order is not sustained in the solid state, the THF-suspended fibres could nevertheless potentially be utilized as a template in nano/micro-fabrication processes.^[2c,28]

Photophysical and light-harvesting properties: In accordance with the zero-generation model compounds, expansion of the π -conjugated system in first-generation dendrimers 9a-c also affords a red-shift of the photophysical properties of the dithienophosphole core. As expected, the three compounds 9a-c show fairly similar absorption and emission maxima at $\lambda_{abs} = 303(\pm 3)$ and $469(\pm 1)$ nm, as well as $\lambda_{em} =$ $551(\pm 7)$ nm (see Table 2). The fluorescence values correlate well with those for the oxidized zero-generation reference compound 5 (Table 1). This supports the meta arrangement of the stilbene units having no impact on the photophysics of the π -system of the core, essentially isolating the branches as independent chromophores. It should be noted that the optical spectrum of 9c shows an additional absorption at $\lambda_{abs} = 379$ nm that also correlates with an additional emission band at $\lambda_{em} = 545$ nm (Figure 3), resulting in a whitish yellow color observed for 9c due to the simultaneous emission of both bands ($\lambda_{em} = 457$ and 545 nm).

FULL PAPER

	λ_{abs}	λ _{ex}	λ_{em}	$\phi_{\mathrm{PL}}{}^{\mathrm{[b]}}$
	[IIII]	[1111]	լոույ	
5 ^[a]	463	461, 491(sh)	551	15.5
9 a ^[a]	304, 470	307, 463(sh), 499	558	22.4
solid state		582	654	
calcd ^[c]	517 (2.26)			
9 b ^[a]	305, 468	309, 462, 498	388, 554	19.0
solid state		582	654	
calcd ^[c]	517 (2.34)			
9 c ^[a]	300, 379, 470	300, 386, 461(sh), 500	457, 545	18.8
solid state		556	659	
calcd ^[c]	412 (0.83), 532 (1.11)			

[a] In 1,2-tetrachloroethane. [b] Quantum yield relative to fluorescein (in 0.01 M KOH/ethanol); $\pm 15\%$, in CH₂Cl₂; excited at 470 nm. [c] Calculated values are vertical excitation energies at the TD-DFT B3LYP/6-31G* level, intensity in brackets.



Figure 3. UV/Vis absorption (top) and fluorescence emission (bottom, excitation at λ_{ex} =305 nm) spectra of compounds **5** and **9a–c**. Intensities are arbitrary for clarity and do not reflect relative relationships between compounds.

When compared to the spectrum of compound **5**, it is evident that the well-matching, low-energy absorptions around $\lambda_{abs} = 470$ nm, as well as the emission around $\lambda_{em} = 550$ nm for compounds **9a–c**, arise from the extended dithienophosphole core. Due to their similar wavelengths, the high-energy absorptions around $\lambda_{abs} = 305$ nm, on the other hand, likely stem from transitions within the stilbene branches, as a corresponding transition is not present in the absorption spectrum of **5**. Importantly, the observed emission around

www.chemeurj.org

 $\lambda_{\rm em}$ =550 nm, when exciting the compounds **9a–c** at about 305 nm, supports the desired ET processes towards the core from the branches that act as independent chromophores. The additional transitions observed for compound **9c**, could probably be attributed to electronic processes involving both the diphenylamino stilbene units and the dithienophosphole core (vide infra).

To determine the light-harvesting efficiency of the branches in compounds 9a-c, we employed the method reported by Melinger, Peng and co-workers for oligo(phenyleneethynylene) (OPE) dendrimers, using steady-state fluorescence measurements.^[29] The efficiency of the energy transfer ($\phi_{\rm ET}$) was obtained by comparison of the absorption and excitation profiles for the compounds 9a-c, with normalized dithienophosphole absorptions, and relating the areas under both curves to one another. The results confirm an energy transfer from the light-harvesting branches to the dithienophosphole core that amount to $\phi_{\rm ET} = 55.7\%$ for **9a**, 40.5% for 9b, and 58.8% for 9c. Although these values are not as high as reported for the OPE dendrimers by Melinger and Peng ($\phi_{\rm ET} = 85-93$ %), they relate fairly well with the values reported by Sanji and Tanaka for their phosphole-cored dendrons (cf. $\phi_{\rm ET}$ dendrimers with "Fréchet-type" <67%).^[20] It should also be noted that compounds 9a-c represent first-generation dendrimers; it is known, however, that the light-harvesting efficiency of dendrimers in general improves with increasing generations,^[8f] and the present results can thus be considered a proof-of-principle study.

Organic π -conjugated molecules with trigonal geometry, as it can be achieved by 1,3,5-substitution of a benzene ring, have also been found to exhibit some nonlinear optical (NLO) properties.^[30] Two-photon absorption (TPA) phenomena are among the most common for these materials. Since the dendrimers **9a–c** exhibit a corresponding substitution pattern at the "zero-generation" benzene ring, we have also looked into the TPA behavior of the three compounds. Using a pulsed Ti:sapphire laser (100 fs), we examined their NLO behavior in dichloroethane by means of two-photon excitation spectroscopy (TPE) upon excitation at 780 nm.^[31] However, although the three dendrimers showed some TPE-behavior, their cross sections were found to be rather small ranging from $\delta = 21.1-26.6$ GM only.

Theoretical calculations: To gain a better understanding of the ET processes observed for the dendrimers 9a-c, as well to find an explanation for the occurrence of an additional set of bands in the optical spectra of 9c, we performed DFT calculations at the B3LYP/6-31G* level of theory, including time-dependent measurements.^[32] The relevant orbitals of the energy-minimized structures are depicted in Figure 4. As can be seen, the HOMO and LUMO of 9a and 9b are similar in shape, and the slight energy variations could be explained through the electronic effect of the terminal CF₃ groups in 9b. Both orbitals represent the extended dithienophosphole core, which is consistent with the optical spectroscopy data obtained for both compounds (vide supra). The same is true for the band gap of both materials amounting

to $E_{bg} = 2.67 \text{ eV}$ for **9a** and 2.66 eV for **9b**. The HOMO-1 and HOMO-2 in both compounds, on the other hand, represent the dendrons and support their nature as independent chromophores. Although slight differences in energy and shape exist between those orbitals, again likely due to the electronic nature of the terminal CF₃ group in 9b, both sets of orbitals are essentially degenerate (9a: $E_{\rm H-1} = -5.559 \, {\rm eV}$, $E_{\text{H}-2} = -5.560 \text{ eV}; \text{ 9b}: E_{\text{H}-1} = -6.009 \text{ eV}, E_{\text{H}-2} = -6.015 \text{ eV}).$ Surprisingly, the orbital sequence in 9c is significantly different. Whereas the LUMO has a similar shape to those of 9a and 9b, a corresponding HOMO orbital is not observed. Due to considerable π -conjugation of the amino nitrogen atoms in the para position, and the resulting loss of symmetry due to the somewhat twisted N-phenyl groups, the bonding orbitals of 9c switch places. We have recently observed behavior for amino-substituted, similar π -extended benzo[1,2-b:5,4-b']dithiophenes.^[33] Consequently, the dendrons are now represented by HOMO and HOMO-1, whereas the extended π -conjugated dithienophosphole core becomes HOMO-2. On the other hand, the band gap of 9c $(E_{\rm bs}=2.58~{\rm eV})$ is not much different from that of **9a** and **9b**, which is in line with the optical spectroscopy data. However, it should be noted in this context that the energy differences between HOMO, HOMO-1, and HOMO-2 in 9c are very small. Again, the orbitals representing the dendrons (HOMO, HOMO-1) are essentially degenerate at $E_{\rm H}$ = -4.832 eV and $E_{\text{H}=1} = -4.834 \text{ eV}$, and the energy of the HOMO-2 is $E_{H-2} = -4.843$ eV. Remarkably, HOMO-2 is not limited to the extended dithienophosphole core; it actually expands throughout a significantly longer segment involving two of the dendrons, including the terminal Nphenyl groups. The additional band in the absorption spectra of 9c can thus be attributed to the altered orbital sequence that also electronically links the dendrons with the core. This is also supported by the TD-DFT calculations that show a notable additional absorption band for 9c at 412 nm resulting from a transition from the branches to the core, whereas the low-energy transition of 9c at 532 nm, as well as the only significant bands for 9a and 9b at 517 nm (for both), are located in the core. As for the emission properties of 9c (Figure 3, bottom), the electronic structure of the dendrons appears to allow for an additional emission coming from these chromophores ($\lambda_{em} = 457 \text{ nm}$), next to the emission from the core at $\lambda_{em} = 545$ nm. It is worth noting that a similar emission feature is also observed for **9b** (λ_{em} = 388, 554 nm), but is much less pronounced (see Figure 3, bottom).

Conclusions

In conclusion, we have functionalized the dithieno[3,2-b:2',3'-d]phosphole scaffold with formyl groups at the 2- and 6-position that allowed for an extension of the π -conjugated system with phenylenevinylene groups through a Wittig-Horner protocol. Studies towards the general accessibility have provided dithienophosphole materials with significant-

4140



Figure 4. Important molecular orbitals and energies of the minimized structures for compounds 9a-c (B3LYP/6-31G* level of theory).

ly reduced band gaps covering the full optical spectrum, depending on the electronic nature of the terminal groups used. Extension of this protocol towards first generation OPV dendrimers has provided a series of dendrimers with electron-withdrawing, -neutral, as well as -donating terminal groups. The nature of the end groups used has been found to have significant impact on the self-organization, but more importantly, also on the optical and energy-transfer properties of the materials. Due to the rigid, planar, extended π system of the phenyl-terminated dendrimer, 9a self-organizes into 1D microfibres in THF, whereas the bulky end groups in 9b and 9c do not seem to allow for extended structures. In terms of optical properties, the three dendrimers show enhanced fluorescence emission from the core ranging between 40% to almost 60% intensity increase, again depending on the end-groups employed. Optical spectroscopy and theoretical DFT-calculations have revealed that the electronic structure of the NPh2-terminated material 9c exhibits some significantly different electronic properties to those observed for the other two dendrimers 9a and 9b, which can be attributed to the electron-donating character of the end-groups in **9c**. These end-groups make the dendrons noticeably strong chromophores, resulting in the occurrence of an additional emission band, next to the (enhanced) emission band from the dithienophosphole core that is common for all three compounds. In summary, the present study has confirmed that the intriguing photophysical properties of the dithienophosphole system can be further improved by embedding this unit as core in π -conjugated dendrimers and we are currently expanding this approach to larger generation OPV dendrimers. We are also targeting the implementation of this core in a variety of other conjugated and non-conjugated dendrimers in the future.

Experimental Section

General procedures: Reactions were carried out in dry glassware and under inert atmosphere of purified argon or nitrogen using Schlenk techniques. Solvents were dried using an MBraun solvent purification system.

www.chemeurj.org

Column chromatography was carried out using silica gel (70-230 mesh, 60 Å) and aluminum oxide (activated, neutral, Brockmann I, standard grade, ≈ 150 mesh, 58 Å). *n*BuLi (2.5 M in hexane), H₂O₂, diethyl benzylphosphonate, and tBuOK were purchased from Aldrich and used as received. LDA was prepared by treating diisopropylamine (freshly distilled) with *n*BuLi in THF at -78°C, and used immediately. Dithieno[3,2-b:2',3'd]phosphole (1),^[16a] diethyl 4-(trifluoromethyl)benzylphosphonate,^[34] diethyl 4-methoxybenzylphosphonate,^[22a] 4-(diphenylamino)-benzylphosphonate,^[22a] and the dendritic carboxylic acids $6a-c^{[24]}$ were prepared by literature methods. ¹H NMR, ¹³C¹H NMR, and ³¹P¹H NMR spectra were recorded on Bruker AC200, Bruker DMX-300, or Bruker DRX-400 spectrometers, respectively. Chemical shifts were referenced to external $85\,\%\,$ H_3PO_4 ($^{31}\text{P})$ or TMS ($^{13}\text{C},\,^{1}\text{H}).$ Elemental analyses were performed at the Department of Chemistry at the University of Calgary. Electron ionization (70 eV) mass spectra were run on a Finigan SSQ 7000 spectrometer, and ionization electrospray in a Bruker Daltonic Esquire 3000 spectrometer. Optical spectroscopy data were recorded using a Jasco FP-6500/6600 spectrofluorometer and UV-Vis-NIR Cary 5000 spectrophotometer. Thermal analyses were performed using a TA-Q200 DSC instrument.

Synthesis of 2: LDA (1.9 mL, 2M in THF) was added to a solution of dithieno[3,2-b:2',3'-d]phosphole (500 mg, 1.84 mmol) in dry THF (40 mL) at -78°C. After 10 min, the volatiles were removed under reduced pressure. Subsequently, THF (40 mL) and DMF (1.4 mL, 18.36 mmol) were added at -78°C. The reaction was stirred 10 min at low temperature. After that, the crude was allowed to reach room temperature and stirred for another 2 h. H₂O was added and the mixture was neutralized with 2 M HCl. The product was extracted with dichloromethane (×3) and dried with MgSO4. The crude was filtrated over neutral alumina, concentrated, and precipitated with pentane to afford a yellow solid (yield: 538 mg, 89%). ¹H NMR (300 MHz, 25°C, CDCl₃): $\delta = 9.93$ (s, 2H; CHO), 7.86 (s, 2H; thiophene), 7.41-7.28 ppm (m, 5H; ArH); ¹³C[¹H] NMR (100 MHz, 25°C, CD₂Cl₂): $\delta = 183.1$ (s, CHO), 152.1 (d, ¹*J*(C,P) = 12.2 Hz, *ipso*-thiophene), 149.0 (s, C-thiophene), 148.2 (d, ²J(C,P)=5.2 Hz, C-thiophene), 136.2 (d, ${}^{2}J(C,P) = 18.6$ Hz, CH-thiophene), 133.3 (d, ${}^{2}J(C,P) = 21.4$ Hz, o-Ph), 131.6 (d, J(C,P)=15.1 Hz, ipso-Ph), 130.9 (s, p-Ph), 129.7 ppm (d, ³J- $(C,P) = 8.3 \text{ Hz}, m-Ph); {}^{31}P{}^{1}H} \text{ NMR} (162 \text{ MHz}, 25 °C, CDCl_3): \delta =$ -19.8 ppm; MS (EI, 70 eV): m/z (%): 328 (100) $[M^+]$, 299 (20) $[M^+]$ -CHO]; elemental analysis calcd (%) for C₁₆H₉O₂PS₂: C 58.53, H 2.76; found: C 58.82, H 2.76.

General Wittig-Horner reaction procedure: Solid *t*BuOK (75 mg, 0.67 mmol) was added in small portions to a solution of **2** (100 mg, 0.3 mmol) and the corresponding phosphonate **3a–d** (0.7 mmol) in THF (50 mL) at -78 °C. After 1 h, the reaction was allowed to reach room temperature and stirred for another 4 h. H₂O was added, and the crude was neutralized with 2M HCl. The product was extracted with CH₂Cl₂, and the organic layer was dried over MgSO₄. After evaporation of the solvent, the crude was purified as indicated in each case (see below):

Compound 4a: Column chromatography: SiO₂, CH₂Cl₂/pentane 1:9; orange solid, yield: 103 mg, 72%; ¹H NMR (300 MHz, 25 °C, CDCl₃): $\delta =$ 7.47–7.44 (m, 5H; ArH), 7.41–7.25 (m, 10H; ArH), 7.21 (d, *J*=16.2 Hz, 2H; 2×*CH*=CH-), 7.18 (s, 2H; thiophene), 6.94 ppm (d, *J*=16.2 Hz, 2H; 2×*CH*=CH-); ¹³Cl¹H} NMR (75 MHz, 25 °C, CD₂Cl₂): $\delta =$ 148.4 (d, ¹*J*-(C,P)=8.5 Hz, *ipso*-thiophene), 145.9 (d, ²*J*(C,P)=6.5 Hz, thiophene), 137.4 (s, thiophene), 132.9 (d, ³*J*(C,P)=20.1 Hz, *o*-Ph), 130.1 (s, Ar), 129.4 (s, Ar), 129.3 (s, Ar), 129.0 (s, Ar), 128.4 (d, ²*J*(C,P)=18.7 Hz, Ar), 126.8 (s, Ar), 126.3 (d, ²*J*(C,P)=19.3 Hz, thiophene), 122.5 ppm (s, Ar); ³¹Pl¹H} NMR (162 MHz, 25 °C, CDCl₃): $\delta =$ –19.9 ppm; elemental analysis calcd (%) for C₃₀H₂₁PS₂: C 75.60, H 4.44; found: C 75.27, H 4.30.

Compound 4b: Column chromatography: SiO₂, CH₂Cl₂/pentane 1:1; orange solid, yield: 109 mg, 67%; ¹H NMR (400 MHz, 25 °C, CD₂Cl₂): δ =7.45–7.40 (m, 6H; ArH), 7.35–7.32 (m, 3H), 7.15 (s, 2H; thiophene), 7.14 (d, *J*=16.0 Hz, 2 H; 2×*CH*=CH-), 6.93–6.89 (m, 6H), 3.84 ppm (s, 6H; 2×O*CH*₃); ¹³C{¹H} NMR (75 MHz, 25 °C, CD₂Cl₂): δ =160.1 (s, Ar), 148.1 (d, ¹*J*(C,P)=8.8 Hz, *ipso*-thiophene), 146.2 (d, ²*J*(C,P)=6.5 Hz, thiophene), 140.7 (s, Ar), 132.9 (d, ²*J*(C,P)=20.4 Hz, *o*-Ph), 130.0 (d, ³*J*-(C,P)=9.9 Hz, *m*-Ph), 129.5 (s, *ipso*-Ph), 129.4 (d, *J*(C,P)=7.6 Hz, Ar), 128.3 (s, *p*-Ph), 128.1 (s, Ar), 128.1 (s, -CH=CH-), 125.5 (d, ²*J*(C,P)=

19.4 Hz, thiophene), 120.4 (s, -CH=CH-), 114.7 (s, Ar), 55.8 ppm (s, -OCH₃); ${}^{31}P{}^{1}H{}$ NMR (162 MHz, 25 °C, CDCl₃): $\delta{}={}-20.0$ ppm; elemental analysis calcd (%) for C₃₂H₂₅O₂PS₂: C 71.62, H 4.70; found: C 71.36, H 4.47.

Compound 4c: Column chromatography: SiO₂, CH₂Cl₂/pentane 1:9; orange solid, yield: 149 mg, 81 %; ¹H NMR (300 MHz, 25 °C, CD₂Cl₂): δ =7.60 (s, 8H; ArH), 7.42–7.30 (m, 7H), 7.24 (s, 2H; thiophene), 6.97 ppm (d, *J*=15.9 Hz, 2H; 2×*CH*=CH-); ¹³C[¹H] NMR (75 MHz, 25 °C, CD₂Cl₂): δ =149.0 (d, ¹*J*(C,P)=9.1 Hz, *ipso*-thiophene), 145.4 (d, ²*J*(C,P)=6.3 Hz, thiophene), 141.0 (s, Ar), 132.0 (d, ²*J*(C,P)=20.4 Hz, *o*-Ph), 130.2 (s, ArH), 129.5 (s, ArH), 129.4 (s, Ar), 127.5 (d, ²*J*(C,P)=19.3 Hz, *o*-thiophene), 127.2 (s, ArH), 126.9 (s, ArH), 126.8 (s, -CH=CH-), 126.2 (q, ³*J*(C,F)=3.7 Hz, ArH), 124.9 (s, -CH=CH-), 124.8 ppm (q, ¹*J*-(C,F)=271.8 Hz, -CF₃); ³¹P[¹H] NMR (162 MHz, 25 °C, CDCl₃): δ = -19.8 ppm; elemental analysis calcd (%) for C₃₂H₁₉F₆PS₂: C 62.74, H 3.13; found: C 62.59, H 3.31.

Compound 4d: Compound **4d** was obtained according to the standard procedure (see above). However, the reaction time was 4 h instead of 1 h at low temperature. Column chromatography: Al₂O₃, CH₂Cl₂/pentane 3:7; red solid, yield: 192 mg, 79%; ¹H NMR (200 MHz, 25 °C, CDCl₃): δ =7.34–7.23 (m, 17H), 7.13–7.01 (m, 20H), 6.84 ppm (d, *J*=16.2 Hz, 2H; 2×*CH*=CH-); ¹³C[¹H] NMR (100 MHz, 25 °C, CD₂Cl₂): δ =148.2 (d, ¹*J*(C,P)=9.1 Hz, *ipso*-thiophene), 148.1 (s, Ar), 148.0 (s, Ar), 147.9 (s, Ar), 136.7 (s, Ar), 132.9 (d, ²*J*(C,P)=20.4 Hz, *o*-Ph), 131.4 (s, Ar), 130.0 (s, Ar), 129.9 (s, ArH), 129.7 (s, ArH), 129.4 (d, ³*J*(C,P)=8.0 Hz, *m*-Ph), 128.1 (s, ArH), 127.7 (s, ArH), 125.7 (d, ²*J*(C,P)=18.8 Hz, ArH), 125.2 (s, ArH), 123.8 (s, ArH), 123.8 (s, ArH), 120.8 ppm (s, ArH); ³¹P[⁴H} NMR (162 MHz, 25 °C, CDCl₃): δ =-20.0 ppm; elemental analysis calcd (%) for C₅₄H₃₉N₂PS₂: C 79.97, H 4.85 N 3.45; found: C 79.85, H 4.77, N 3.59.

Compound 5: H₂O₂ (0.5 mL, 30 % w.t. in water) was added dropwise into a solution of compound 4a (50 mg, 0.1 mmol) in CH₂Cl₂ (30 mL). The reaction was stirred for 3 h at room temperature. The crude was washed with H2O and dried over MgSO4. Precipitation from CH2Cl2/hexanes, afforded an orange solid (yield: 47 mg, 96%). ¹H NMR (400 MHz, 25°C, CD_2Cl_2): $\delta = 7.76$ (dd, J = 14.8 Hz, J = 7.6 Hz, 2H; o-PPh), 7.57 (tq, J =7.6 Hz, J=3.2 Hz, 1 H; p-PPh), 7.48–7.44 (m, 6H; Ar), 7.36 (t, J=7.2 Hz, 4H; Ar), 7.28 (tt, J=7.2 Hz, J=1.2 Hz, 2H; Ar), 7.19 (d, J=16.4 Hz, 2H; -CH=CH-), 7.12 (d, J=2.8 Hz, 2H; thiophene), 6.96 ppm (d, J= 16 Hz, 2H; -CH=CH-); ${}^{13}C{}^{1}H$ NMR (100 MHz, 25 °C, CD₂Cl₂): $\delta =$ 148.1 (s, thiophene), 147.9 (s, thiophene), 144.3 (s, thiophene), 139.3 (d, ${}^{1}J(C,P) = 3.9 \text{ Hz}; \text{ Ar}), 136.9 (s, \text{ Ar}), 133.1 (d, J(C,P) = 2.7 \text{ Hz}; \text{ ArH}), 131.4$ (d, J(C,P)=11.5 Hz; o-P), 130.0 (s; ArH), 129.6 (s; ArH), 129.5 (s, ArH), 129.4 (s, Ar), 128.7 (s, ArH), 127.0 (s, ArH), 124.8 (d, J(C,P)=14.2 Hz; o-P), 121.6 (s, ArH) ppm; ${}^{31}P{}^{1}H$ NMR (162 MHz, 25 °C, CD₂Cl₂): $\delta =$ 18.6 ppm; HRMS calcd for $C_{30}H_{21}POS_2$ [*M*⁺]: 492.0771; found: 492.0754.

General procedure for the dendritic benzyl alcohols: LiAlH₄ (7.12 mL, 1 μ in THF) was added dropwise to a solution of the corresponding dendritic carboxylic acid $6a-e^{[24]}$ (3.24 mmol) dissolved in THF (100 mL) at 0 °C. After 1 h, the reaction was allowed to reach room temperature and stirred for another hour. The reaction mixture was then quenched with water and neutralized with 2 μ HCl. The organic solvent was removed and the precipitate formed was filtrated and purified as indicated in each case, as follows:

Compound 7a: The collected white precipitate was spectroscopically pure and used for the next step without further purification (yield: 930 mg, 92 %). ¹H NMR (400 MHz, 25 °C, $[D_6]$ acetone): $\delta = 7.73$ (br

s, 1H; ArH), 7.63 (d, 4H; J=7.6 Hz; ArH), 7.53 (brs, 2H; ArH), 7.39 (t, 4H; J=7.6 Hz; ArH), 7.32–7.26 (m, 6H; ArH), 4.70 ppm (brs, 2H; -CH₂-OH); ¹³C[¹H] NMR (100 MHz, 25 °C, [D₆]acetone): δ =145.3 (s; Ar), 139.7 (s, Ar), 139.4 (s, Ar), 130.7 (s, ArH), 130.6 (s, 4×ArH), 130.4 (s, ArH), 129.5 (s, ArH), 128.4 (s, 4×ArH), 125.8 (s, ArH), 125.3 (s, ArH), 65.5 ppm (s, -CH₂OH) ppm; MS (EI, 70 eV) *m/z* (%): 312 (100) [*M*⁺].

Compound 7b: The precipitate was washed with ethanol affording a white solid (yield: 1.29 g, 89%). ¹H NMR (500 MHz, 25 °C, CDCl₃): $\delta =$ 7.62 (s, 8H; ArH), 7.59 (s, 1H; ArH), 7.50 (s, 2H; ArH), 7.23 (d, 2H; J = 16.5 Hz; -CH=CH-), 7.19 (d, 2H; J = 16.5 Hz; -CH=CH-), 3.20 (d, 2H; J = 5.5 Hz; -CH₂OH) ppm; ¹³C[¹H] NMR (100 MHz, 25 °C, CD₂Cl₂): $\delta =$

4142 ·

147.4 (s, Ar), 143.0 (s, Ar), 141.4 (s, Ar), 138.0 (s, Ar), 131.3 (s, $2 \times ArH$), 128.3 (s, ArH), 127.3 (s, $4 \times ArH$), 126.2 (q, J(C,F)=3.9 Hz; $4 \times ArH$), 125.4 (s, $2 \times ArH$), 125.0 (s, ArH), 65.3 ppm (s, -CH₂OH); MS (EI, 70 eV): m/z (%): 448 (100) [M^+].

Compound 7c: The precipitate was washed with hot ethanol affording a yellow solid (yield: 1.80 g, 86%). ¹H NMR (400 MHz, 25°C, [D₆]acetone): δ =7.66 (brs, 1H; ArH), 7.54 (d, 4H; *J*=8.5 Hz; ArH), 7.49 (brs, 2H; ArH), 7.34–7.30 (m, 7H; ArH), 7.27 (d, 2H; *J*=16.5 Hz; -*CH*=CH-), 7.17 (d, 2H; *J*=16.5 Hz; -*CH*=CH-), 7.10–7.60 (m, 13 H; Ar), 7.02 (d, 4H; *J*=8.5 Hz; ArH), 4.68 ppm (d, 2H; *J*=6.0 Hz; -*CH*₂OH); ¹³C[¹H] NMR (100 MHz, 25°C, [D₆]acetone): δ =149.5 (s, Ar), 149.3 (s, Ar), 145.2 (s, Ar), 139.9 (s; Ar), 133.7 (s, Ar), 131.3 (s, 8×ArH), 130.1 (s, ArH), 129.4 (s, 4×ArH), 128.9 (s; ArH), 126.3 (s, 8×ArH), 125.4 (s, Ar), 125.2 (s, 4×ArH), 125.1 (s, CH, 4×ArH), 125.0 (s, ArH), 65.5 ppm (s, -*C*H₂OH); MS (EI, 70 eV): *m/z* (%): 646 (100) [*M*⁺].

General procedure for the dendritic phosphonates: Iodine (1.1 equiv) was added to a mixture of the corresponding benzylic alcohol 7a-c (1 equiv) and triethyl phosphite (2 mL) at 0 °C. After stirring for 10 min at low temperature, the crude reaction mixture was allowed to reach room temperature. The reaction was stirred 2 h and heated to reflux for a further 5 h at 140 °C. The excess of triethyl phosphite was removed under vacuum. The product was purified as indicated in each case, as follows:

Compound 8a: The solid was crystallized from ethyl acetate/hexanes affording a white solid (yield: 552 mg, 72%). ¹H NMR (400 MHz, 25°C, [D₆]acetone): δ = 7.73 (brs 1H; ArH), 7.63 (d, 4H; *J* = 7.6 Hz; ArH), 7.49 (brs, 2H; ArH), 7.39 (t, 4H; *J* = 7.6 Hz; ArH), 7.31–7.24 (m, 6H; ArH), 4.04 (q, 4H; *J* = 7.2 Hz; O-CH₂-CH₃), 3.23 (d, 2H; *J* = 21.6 Hz; -CH₂-P), 1.23 ppm (t, 6H; *J* = 7.2 Hz; O-CH₂-CH₃); ¹³C[¹H] NMR (100 MHz, 25°C, CDCl₃): δ = 139.8 (d, *J* = 2.9 Hz; Ar), 139.3 (s, Ar), 135.3 (d, *J* = 9.2 Hz; Ar), 130.9 (s, ArH), 130.6 (s, 4×ArH), 130.1 (s, ArH), 129.5 (s, ArH), 129.2 (s, *J* = 6.7 Hz; ArH), 128.4 (s, 4×ArH), 125.0 (d, *J* = 3.0 Hz; ArH), 63.4 (d, *J* = 6.8 Hz; 2×OCH₂CH₃); ³¹P[¹H] NMR (162 MHz, 25°C, CDCl₃): δ = 26.1 ppm; MS (EI, 70 eV): *m/z* (%): 432 (55) [*M*⁺].

Compound 8b: The crude product was washed several times with hexanes affording a light yellow solid (yield: 500 mg, 88%). ¹H NMR (300 MHz, 25°C, CDCl₃): δ =7.62 (s, 8H; ArH), 7.57 (brs, 1H; ArH), 7.43 (s, 2H; ArH), 7.18 (s, 4H; *-CH*=CH-), 4.07 (q, 4H; *J*=4.9 Hz; O-*CH*₂-CH₃), 3.20 (d, 2H; *J*=21.6 Hz; *-CH*₃P), 1.28 ppm (t, 6H; *J*=4.9; O-CH₂-CH₃); ¹³Cl¹H} NMR (100 MHz, 25°C, CDCl₃): δ =140.5 (d, *J*= 1.4 Hz; Ar), 137.4 (d, *J*=3.0 Hz; Ar), 132.8 (d, *J*=3.0 Hz; Ar), 130.5 (s, ArH), 129.5 (q, *J*=32.6 Hz; Ar), 127.9 (s, ArH), 127.9 (s, Ar), 126.6 (s, 4×ArH), 125.7 (q, *J*=3.7 Hz; 4×ArH), 123.9 (d, *J*=3.5 Hz; ArH), 122.6 (s, Ar), 62.3 (d, *J*=6.8 Hz; 2×OCH₂CH₃); ³¹P[¹H} NMR (162 MHz, 25°C, CDCl₃): δ =25.0 ppm; MS (EI, 70 eV): *m/z* (%): 568 (100) [*M*⁺].

Compound 8c: The crude was washed several times with hexanes affording a yellow solid (yield: 706 mg, 92%). ¹H NMR (300 MHz, 25°C, CDCl₃): δ =7.53 (brs, 1H; ArH), 7.42 (d, 4H; *J*=8.7 Hz; ArH), 7.30–7.25 (m, 10H; ArH), 7.12–7.02 (m, 20H; ArH), 4.03 (q, 4H; *J*=4.9 Hz; O-*CH*₂CH₃), 3.20 (d, 2H; *J*=21.6 Hz; -*CH*₂P), 1.28 ppm (t, 6H; *J*=4.9; O-CH₂CH₃); ¹³C[¹H] NMR (100 MHz, 25°C, CDCl₃): δ =149.4 (s, Ar), 149.3 (s; Ar), 140.0 (d, *J*=2.8 Hz; Ar), 135.1 (d, *J*=9.0 Hz; Ar), 133.5 (s, ArH), 131.3 (s, 8×ArH), 130.2 (s, ArH), 129.4 (s, 4×ArH), 128.7 (s, ArH), 128.6 (s, ArH), 128.6 (s, ArH), 126.3 (s, 8×ArH), 128.1 (d, *J*=7.5 Hz; ArH), 124.7 (s; ArH), 63.3 (d, *J*=6.6 Hz; 2×OCH₂CH₃); ³¹P[¹H] NMR (162 MHz, 25°C, CDCl₃): δ =26.6 ppm; MS (EI, 70 eV): *m/z* (%): 767 (100) [*M*⁺].

General procedure for the dendrimer synthesis: Solid *t*BuOK (74 mg, 0.66 mmol) was added in small portions to a solution of **2** (100 mg, 0.3 mmol) and the corresponding phosphonate (0.7 mmol) in THF (30 mL) at -78 °C. After 8 h, the reaction was allowed to reach room temperature and stirred for another 4 h. H₂O was added, and the crude reaction mixture was neutralized with 2M HCl. The product was oxidized in situ by treatment with H₂O₂ (1 mL) and stirred overnight. The dendrimers were worked up as indicated in each case, as follows:

Compound 9a: After the oxidation, the reaction was quenched with water and the THF removed. The resulting red solid was filtered and washed with diethyl ether, acetone and ethanol (yield: 144 mg, 53%). ¹H NMR (400 MHz, 25 °C, $C_2D_4Cl_2$): δ = 7.80 (dd, J = 13.2 Hz, J = 8.0 Hz, 2 H; *o*-Ph), 7.59–7.53 (m, 17 H), 7.42 (tq, J = 7.2 Hz, J = 3.2 Hz; 8H), 7.34–7.30 (m, 5H; Ar), 7.26–7.14 (m, 11 H; Ar), 7.00 ppm (d, J = 16 Hz, 2 H; -CH=*CH*-); ¹³C{¹H} NMR (100 MHz, 25 °C, $C_2D_4Cl_2$): δ = 147.1 (s, thiophene), 147.0 (s, thiophene), 143.9 (s, Ar), 130.7 (d, J(C,P)=11.7 Hz; Ar), 129.5 (s, Ar), 128.9 (d, J(C,P)=13.3 Hz; Ar), 128.7 (s, ArH), 127.9 (s, ArH), 124.6 (d, J(C,P)=14.2 Hz; Ar), 124.3 (s, ArH), 123.7 (s; ArH), 121.6 (s, Ar), 120.6 ppm (s, Ar); ³¹P{¹H} NMR (162 MHz, 25 °C, $C_2D_2Cl_4$): δ = 19.8 ppm; MS (ESI, positive ions): m/z: 901.13 [M+H⁺]; HRMS calc for $C_{62}H_{45}N_4OPS_2$ [M^+]: 900.2649; found: 900.2614.

Compound 9b: Once the crude was oxidized, the final product was purified by column chromatography (SiO₂, eluent: from CHCl₃/THF 10:0 to CHCl₃/THF 1:9), giving a red solid (yield: 152 mg, 43%). ¹H NMR (400 MHz, 25 °C, CD₂Cl₂): δ = 7.79 (dd, *J*=13.2 Hz, *J*=7.2 Hz, 2 H; *o*-Ph), 7.69–7.57 (m, 21 H), 7.48 (dt, *J*=8.0 Hz, *J*=3.2 Hz, 2 H; *m*-Ph), 7.30 (d, *J*=16.0 Hz, 2H; -CH=*CH*-), 7.25 (s, 8H; Ar), 7.19 (d, *J*=2.4 Hz, 2H; thiophene), 7.0 ppm (d, *J*=16.0 Hz, 2H; -CH=*CH*-); ¹³Cl¹H} NMR (100 MHz, 25 °C, C₂D₄Cl₂): δ =144.9 (s, Ar), 141.9 (s, Ar), 140.5 (s, Ar), 137.7 (s, Ar), 137.3 (s, Ar), 136.7 (s, Ar), 130.9 (s, Ar), 130.4 (s, Ar), 125.0 (s, Ar), 124.7 (s, Ar), 122.9 (s, Ar), 120.0 ppm (s, Ar); ³¹Pl¹H] NMR (162 MHz, 25 °C, C₂D₄Cl₄): δ =13.4 ppm; MS (ESI, positive ions): *m*/z: 1173.00 [*M*⁺+H], 1196.02 [*M*⁺+Na]; elemental analysis calcd (%) for C₆₆H₄₁F₁₂OPS₂: C 67.57, H 3.52; found: C 67.96, H 3.11.

Compound 9c: After oxidation, the final compound was purified by column chromatography (SiO2, eluent: from CH2Cl2/acetone 9.9:0.1 to CH₂Cl₂/acetone 9:1), giving a red solid (yield: 172 mg, 49%). ¹H NMR (400 MHz, 25 °C, CD₂Cl₂): $\delta = 7.78$ (dd, J = 13.2 Hz, J = 7.6 Hz, 2H; o-PPh), 7.59-7.54 (m, 3H; Ar), 7.47-7.42 (m, 11H; Ar), 7.28 (t, J=8.0 Hz, 18H), 7.19–7.01 (m, 45H; Ar), 7.98 ppm (d, J=16.0 Hz, 2H; -CH=CH-); ¹³C{¹H} NMR (100 MHz, 25 °C, CD₂Cl₂): $\delta = 159.0$ (s, Ar), 148.2 (s, Ar), 148.1 (s, ArH), 144.4 (s, Ar), 139.1 (s, Ar), 137.7 (s, Ar), 133.1 (s, Ar), 131.7 (s, Ar), 131.4 (d, J(C,P)=11.0 Hz; Ar), 130.2 (s, Ar), 129.9 (s, ArH), 129.7 (s, Ar), 129.6 (s, Ar), 128.0 (s, ArH), 126.8 (s, Ar), 126.5 (s, Ar), 125.2 (s, Ar), 124.4 (s, Ar), 123.9 (s, ArH), 123.8 (s, ArH), 120.1 (s, Ar), 121.7 ppm (s, Ar); ${}^{31}P{}^{1}H{}$ NMR (162 MHz, 25 °C, CD₂Cl₂): $\delta =$ 18.3 ppm; MS (ESI, positive ions): m/z: 1569.23 [M⁺+H], 1592.25 [M⁺ +Na], 1607.21 $[M^++K]$; elemental analysis calcd (%) for C₁₁₀H₈₁N₄OPS₂: C 84.15, H 5.70, N 3.57; found: C 84.28, H 5.55, N 3.17.

Acknowledgements

Financial support by Natural Sciences and Engineering Research Council (NSERC) of Canada, MEC of Spain (projects CTQ2006-08871 and NAN2004-08843-C05-02), and Junta de Comunidades de Castilla-La Mancha (project PCI08-0033) is gratefully acknowledged. C.R.N. thanks Junta de Comunidades de Castilla-La Mancha for a scholarship. T.B. thanks Alberta Ingenuity for a New Faculty Award. We also thank Dr. J. Konu for the X-ray data collection, as well as Prof. D. T. Cramb and K. Yaehne for the TPE measurements.

- [1] a) Conjugated Conducting Polymers, Vol.102 (Ed.: H. Kiess), Springer, New York, 1992; b) H. S. Nalwa, Handbook of Conductive Materials and Polymers, Wiley, New York, 1997; c) Handbook of Conducting Polymers, 3rd ed. (Eds.: T. A. Skotheim, J. R. Reynolds), CRC, Boca Raton, 2006.
- [2] a) K. Müllen, G. Wegner, *Electronic Materials: The Oligomer Approach*, Wiley-VCH, Weinheim, **1998**; b) P. F. H. Schwab, J. R. Smith, J. Michl, *Chem. Rev.* **2005**, *105*, 1197; c) F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer, A. P. H. J. Schenning, *Chem. Rev.* **2005**, *105*, 1491; d) J. Roncali, *Chem. Rev.* **1997**, *97*, 173.

CHEMISTRY

- [3] Handbook of Oligo- and Polythiophenes (Ed.: D. Fichou), Wiley-VCH, Weinheim, 1998.
- [4] Organic Light Emitting Devices (Eds.: K. Müllen, U. Scherf), Wiley-VCH, Weinheim, 2005.
- [5] a) C. D. Dimitrakopoulos, P. R. L. Malenfant, Adv. Mater. 2002, 14, 99; b) J. E. Anthony, Angew. Chem. 2008, 120, 460; Angew. Chem. Int. Ed. 2008, 47, 452; c) A. R. Murphy, J. M. J. Fréchet, Chem. Rev. 2007, 107, 1066; d) J. Zaumseil, H. Sirringhaus, Chem. Rev. 2007, 107, 1296; e) S. Allard, M. Forster, B. Souharce, H. Thiem, U. Scherf, Angew. Chem. 2008, 120, 4138; Angew. Chem. Int. Ed. 2008, 47, 4070.
- [6] a) B. C. Thompson, J. M. J. Fréchet, Angew. Chem. 2008, 120, 62; Angew. Chem. Int. Ed. 2008, 47, 58; b) S. Günes, H. Neugebauer, N. S. Sariciftci, Chem. Rev. 2007, 107, 1324.
- [7] a) S. W. Thomas III, G. D. Joly, T. M. Swager, *Chem. Rev.* 2007, 107, 1339; b) D. T. McQuade, A. E. Pullen, T. M. Swager, *Chem. Rev.* 2000, 100, 2537.
- [8] See for example: a) S. Rosenfeldt, N. Dingenouts, D. Pötschke, M. Ballauff, A. J. Berresheim, K. Müllen, P. Lindner, Angew. Chem. 2004, 116, 111; Angew. Chem. Int. Ed. 2004, 43, 109; b) U. M. Wiesler, A. J. Berresheim, F. Morgenroth, G. Lieser, K. Müllen, Macromolecules 2001, 34, 187; c) C. Xia, X. Fan, J. Locklin, R. C. Advincula, A. Gies, W. Nonidez, J. Am. Chem. Soc. 2004, 126, 8735; d) C.-Q. Ma, M. Fonrodona, M. C. Schikora, M. M. Wienk, R. A. J. Janssen, P. Bäuerle, Adv. Funct. Mater. 2008, 18, 3323; e) K. R. J. Thomas, T.-H. Huang, J. T. Lin, S.-C. Pu, Y.-M. Cheng, C.-C. Hsieh, C. P. Tai, Chem. Eur. J. 2008, 14, 11231; f) S.-C. Lo, P. L. Burn, Chem. Rev. 2007, 107, 1097; g) P. L. Burn, S.-C. Lo, I. D. W. Samuel, Adv. Mater. 2007, 19, 1675.
- [9] J. C. García-Martínez, E. Díez-Barra, J. Rodríguez-López, Curr. Org. Synth. 2008, 5, 267.
- [10] a) E. Díez-Barra, J. C. García-Martínez, S. Merino, R. del Rey, J. Rodríguez-López, P. Sánchez-Verdú, J. Tejeda, J. Org. Chem. 2001, 66, 5664; b) J. Tolosa, C. Romero-Nieto, E. Díez-Barra, P. Sánchez-Verdú, J. Rodríguez-López, J. Org. Chem. 2007, 72, 3847.
- [11] a) M. G. Hobbs, T. Baumgartner, *Eur. J. Inorg. Chem.* 2007, 3611;
 b) T. Baumgartner, R. Réau, *Chem. Rev.* 2006, *106*, 4681 (Correction: T. Baumgartner, R. Réau, *Chem. Rev.* 2007, *107*, 303); c) F. Mathey, *Angew. Chem.* 2003, *115*, 1616; *Angew. Chem. Int. Ed.* 2003, *42*, 1578; d) D. P. Gates, *Top. Curr. Chem.* 2005, *250*, 107; e) Z. Jin, B. L. Lucht, *J. Organomet. Chem.* 2002, *653*, 167.
- [12] a) Phosphorus: The Carbon Copy (Eds.: K. Dillon, F. Mathey, J. F. Nixon), Wiley, New York, **1998**; b) Houben Weyl, Methods of Organic Chemistry, Vol. E1 & E2: Organic Phosphorous compounds I & II (Ed.: M. Regitz), Thieme, Stuttgart, **1982**; c) F. Mathey, A. Sevin, Molecular Chemistry of the Transition Metals; Wiley, New York, **1996**.
- [13] a) W. Schäfer, A. Schweig, F. Mathey, J. Am. Chem. Soc. 1976, 98, 407; b) E. Mattmann, F. Mathey, A. Sevin, G. Frison, J. Org. Chem. 2002, 67, 1208; c) E. Mattmann, F. Mercier, L. Ricard, F. Mathey, J. Org. Chem. 2002, 67, 5422; d) L. Nyulászi, O. Holloczki, C. Lescop, M. Hissler, R. Réau, Org. Biomol. Chem. 2006, 4, 996; e) D. Delaere, P.-T. Nguyen-Nguyen, M. T. Nguyen, Chem. Phys. Lett. 2004, 383, 138; f) E. Mattmann, D. Simonutti, L. Ricard, F. Mercier, F. Mathey, J. Org. Chem. 2001, 66, 755.
- [14] a) C. Hay, D. Le Vilain, V. Deborde, L. Toupet, R. Réau, Chem. Commun. 1999, 345; b) C. Hay, C. Fischmeister, M. Hissler, L. Toupet, R. Réau, Angew. Chem. 2000, 112, 1882; Angew. Chem. Int. Ed. 2000, 39, 1812; c) C. Hay, M. Hissler, C. Fischmeister, J. Rault-Berthelot, L. Toupet, L. Nyulászi, R. Réau, Chem. Eur. J. 2001, 7, 4222; d) C. Fave, M. Hissler, T. Kárpáti, J. Rault-Berthelot, V. Deborde, L. Toupet, L. Nyulászi, R. Réau, J. Am. Chem. Soc. 2004, 126, 6058; e) V. Lemau de Talance, M. Hissler, L.-Z. Zhang, T. Kárpáti, L. Nyulászi, D. Caras-Quintero, P. Bäuerle, R. Réau, Chem. Commun. 2008, 2200.
- [15] a) C. Fave, T.-Y. Cho, M. Hissler, C.-W. Chen, T.-Y. Luh, C.-C. Wu, R. Réau, J. Am. Chem. Soc. 2003, 125, 9254; b) H.-C. Su, O. Fadhel, C.-J. Yang, T.-Y. Cho, C. Fave, M. Hissler, C.-C. Wu, R. Réau, J. Am. Chem. Soc. 2006, 128, 983.

- [16] a) T. Baumgartner, T. Neumann, B. Wirges, Angew. Chem. 2004, 116, 6323; Angew. Chem. Int. Ed. 2004, 43, 6197; b) T. Baumgartner, W. Bergmans, T. Kárpáti, T. Neumann, M. Nieger, L. Nyulászi, Chem. Eur. J. 2005, 11, 4687.
- [17] a) T. Neumann, Y. Dienes, T. Baumgartner, Org. Lett. 2006, 8, 495; b) Y. Dienes, S. Durben, T. Kárpáti, T. Neumann, U. Englert, L. Nyulászi, T. Baumgartner, Chem. Eur. J. 2007, 13, 7487; c) Y. Dienes, M. Eggenstein, T. Kárpáti, T. C. Sutherland, L. Nyulászi, T. Baumgartner, Chem. Eur. J. 2008, 14, 9878.
- [18] a) A. Fukazawa, M. Hara, T. Okamoto, E.-C. Son, C. Xu, K. Tamao, S. Yamaguchi, Org. Lett. 2008, 10, 913; b) A. Fukazawa, H. Yamada, S. Yamaguchi, Angew. Chem. 2008, 120, 5664; Angew. Chem. Int. Ed. 2008, 47, 5582.
- [19] a) Y. Matano, T. Miyajima, H. Imahori, Y. Kimura, J. Org. Chem. **2007**, 72, 6200; b) T. Miyajima, Y. Matano, H. Imahori, Eur. J. Org. Chem. **2008**, 255; c) Y. Matano, T. Miyajima, T. Fukushima, H. Kaji, Y. Kimura, H. Imahori, Chem. Eur. J. **2008**, 14, 8102.
- [20] T. Sanji, K. Shiraishi, M. Tanaka, Org. Lett. 2007, 9, 3611.
- [21] Crystal data for **2**: (C₁₆H₉O₂PS₂): M_r =328.32, T=173(2) K, triclinic, space group $P\bar{1}$, a=7.5732(15), b=9.5380(19), c=10.567(2) Å, α = 88.99(3), β =75.24(3), γ =81.28(3)°, V=729.4(3) Å³, Z=2, ρ_{calcd} = 1.495 Mgm⁻³, μ =0.474 mm⁻¹, λ =0.71073 Å, $2\theta_{max}$ =50.06°, 4708 measured reflections, 2549 [R(int)=0.0191] independent reflections, GOF on F^2 =1.047, R_1 =0.0288, wR_2 =0.0724 [$I > 2\sigma(I)$], R_1 =0.0315, wR_2 =0.0742 (for all data), largest difference peak and hole 0.294 and -0.245 e Å⁻³. The intensity data were collected on a Nonius KappaCCD diffractometer with graphite monochromated Mo_{Ka} radiation. The structure was solved by direct methods (SHELXTL) and refined on F^2 by full-matrix least-squares techniques. Hydrogen atoms were included by using a riding model. CCDC 690741 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif
- [22] a) S. Zheng, S. Barlow, T. C. Parker, S. R. Marder, *Tetrahedron Lett.* **2003**, 44, 7989; b) A. K. Mohanakrishnan, M. V. Lakshmikantham, M. P. Cava, *Sulfur Lett.* **1998**, 21, 247.
- [23] S. Durben, D. Nickel, R. A. Krüger, T. C. Sutherland, T. Baumgartner, J. Polym. Sci. Part A 2008, 46, 8179.
- [24] J. C. García-Martínez, C. Atienza, M. de La Peña, A. C. Rodrigo, J. Tejeda, J. Rodríguez-López, J. Mass Spectrom. 2009, DOI: 10.1002/ jms.1534.
- [25] A. K. Bhattacharya, G. Thyagarajan, Chem. Rev. 1981, 81, 415.
- [26] L. Zang, Y. Che, J. S. Moore, Acc. Chem. Res. 2008, 41, 1596, and references therein.
- [27] a) A. Ajayaghosh, V. K. Praveen, Acc. Chem. Res. 2007, 40, 644;
 b) A. Ajayaghosh, V. K. Praveen, C. Vijayakumar, Chem. Soc. Rev. 2008, 37, 109;
 c) S. S. Babu, V. K. Praveen, S. Prasanthkumar, A. Ajayaghosh, Chem. Eur. J. 2008, 14, 9577.
- [28] a) A. del Campo, E. Arzt, *Chem. Rev.* **2008**, *108*, 911; b) B. D. Gates, Q. Xu, M. Stewart, D. Ryan, C. G. Willson, G. M Whitesides, *Chem. Rev.* **2005**, *105*, 1171.
- [29] J. S. Melinger, Y. Pan, V. D. Kleiman, Z. Peng, B. L. Davis, D. McMorrow, M. Lu, J. Am. Chem. Soc. 2002, 124, 12002.
- [30] a) S. Barlow, S. R. Marder in: Organic Functional Materials (Eds.: T. J. J. Müller, U. H. F. Bunz), Wiley-VCH, Weinheim, 2006; b) S. R. Marder, Chem. Commun. 2006, 131.
- [31] a) R. L. Goyan, D. T. Cramb, *Photochem. Photobiol.* 2000, 72, 821;
 b) D. A. Oulianov, I. V. Tomov, A. S. Dvornikov, P. M. Rentzepis, *Opt. Commun.* 2001, 191, 235;
 c) J. L. Swift, R. Heuff, D. T. Cramb, *Biophys. J.* 2006, 90, 1396.
- [32] Gaussian 03, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W.

4144 -

© 2009 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Chem. Eur. J. 2009, 15, 4135-4145

Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W.

Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian Inc., Wallingford, CT, 2004.

- [33] M. P. Boone, Y. Dienes, T. Baumgartner, Arkivoc 2009, 90.
- [34] H. K. Shim, I. N. Kang, M. S. Jang, T. Zyung, S. D. Jung, *Macromolecules* 1997, 30, 7749.

Received: November 27, 2008 Published online: March 12, 2009