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White Organic Light-Emitting Diodes Based on Quench-Resistant Fluorescent Organophosphorus Dopants

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The control of the doping ratio of a blue-emitting matrix by an orange emitter with high accuracy still remains very challenging in the development of reproducible white organic light-emitting diodes (WOLEDs). In this work, the development of an organophosphorus dopant that presents a high doping rate in order to reach white emission is reported. The increase of the doping rate has a small impact on the CIE co-ordinates and on the EQE. These results are very appealing towards the development of "easy-to-make" WOLEDS.

1. Introduction

The field of organic optoelectronics has witnessed tremendous progress since the first report on organic light-emitting diodes (OLEDs) by Tang and VanSlyke in 1987.^[1] Taking advantage of the optical/semiconducting properties of π -conjugated organic materials, and also of their lightness and flexible behavior, innovative devices including OLEDs (full-color flat-panel displays) and photovoltaic cells have recently been commercialized.^[2] Among all of the possible applications of organic devices, white organic light-emitting diodes (WOLEDs) have received considerable interest due to their potential for replacing conventional lighting sources for display backlighting and solid-state lighting.^[3] In particular, WOLEDs have the potential to save a significant amount of energy, compared with typical incandescent or fluorescent light bulbs, and therefore are attractive devices in the frame of "sustainable development".^[3a-c] To realize white emission with chromaticity Commission Internationale de l'Eclairage (CIE) co-ordinates close to (0.313, 0.329), various strategies have been developed.^[2a,3] An appealing approach is

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the use of a single chromophore that can combine emission from both monomeric (blue) and aggregate (orange) forms.^[3a,b,4] However, the most-general approaches of obtaining white emission are through combining different organic components emitting: i) three primary colors (red (R), green (G) and blue (B)),^[3,5] or ii) two complementary colors.^[3a,6] This latter approach is more suitable from a practical point of view, since it simply involves the coevaporation of a matrix (generally a suitable dopant.

blue-emitter) with a suitable dopant.

The emissive materials used in WOLEDs can be fluorescent and/or phosphorescent chromophores. Up to now, efficient blue-emitting materials have been most-exclusively fluorescent derivatives, due the short operational lifetimes of blue phosphors.^[7] In contrast, phosphors are the most-investigated dopants, since they can achieve high internal quantum efficiency by employing the participation of the triplet emission.^[8] However, WOLEDs using phosphorescent dopants typically suffer from color-stability problems associated with significant roll-off at high brightness (i.e., high current density) due to strong triplet-triplet or triplet-charge annihilation.^[8d,9] At the moment, the most-widely used phosphorescent emitters are metal complexes of iridium and platinum ions. These precious metals are quite rare and already widely used for many other important industrial applications including homogeneous/heterogeneous catalysis and electronics. Therefore, considering their rarity and their quite-confined geographic localization, the price of these precious metals is continuously increasing (+100% within the last year for Pt and Ir). Indeed, the price and availability of these metal-based phosphors can be a limitation for the long-term mass production of WOLEDs since it seems technologically difficult to recycle these dopants. Therefore, the development of fluorescent WOLEDs is still important for "lowcost" applications, although they are intrinsically less efficient than WOLEDs incorporating phosphorescent dopants.

Considering the most-simple device configuration for WOLEDs (i.e., a blue-emitting matrix doped with a fluorescent compound), one of the most-critical parameters to optimize is the doping rate (DR). In practice, the effective DR required to obtain white emission is usually very low (0.2–2%) and has to be precisely controlled ($\pm 0.1\%$).^[10] Furthermore, besides emission-color modification, small DR variations usually induce dramatic modifications of the device performance, and especially important, a decrease of the external quantum efficiency (EQE).^[10] Controlling these rather-low DRs with a high accuracy

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Figure 1. Chemical structures of the OLED components and dopant A.

is very challenging from an experimental point of view, especially in an industrial process, making matrix doping by no means a trivial task. This severe drawback can strongly limit the repeatability of devices that have identical performances in mass production. Therefore, the design of new, advanced dopants affording WOLEDs presenting a very-small sensitivity to concentration variations is of considerable importance. Materials exhibiting this appealing property are extremely rare for OLEDs^[11] and totally unknown for WOLED applications.

In order to tackle this problem, we decided to exploit the flexibility available for fine-tuning of the optical and electrochemical properties of phosphole-based conjugated systems through manipulation of their chemical structure for the preparation of tailored white-light-emitting devices. We recently showed that bis(2-(5-methyl)thienyl)thioxophosphole, **A**, (**Figure 1**) is an efficient fluorescent dopant for 4,4'-bis(2,2'-diphenylvinyl)biphenyl (DPVBi) (Figure 1) in the construction of WOLEDs that have simplified structures.^[12] These single-emitting layered devices are easily obtained by coevaporation of the two compounds. As usually observed with this general approach, a drawback is that the DRs for obtaining white emission with these phosphole-based molecules are low (approximately 0.1%), and therefore they are quite difficult to control and reproduce within the coevaporation process. Therefore, molecular engineering around the phosphole building block was undertaken, with the preparation of new, advanced, mixed thiophene-phosphole-fluorene dopants.

In this paper, we report on the synthesis and characterization of mixed thiophene-phosphole-fluorene derivatives that can be used as dopants for DPVBi (Figure 1), a widely used blue-emitting matrix. Their chemical structures were elucidated using ¹H-NMR and ¹³C-NMR spectroscopy and mass spectrometry. Their photophysical, thermal and electrochemical properties were determined using UV–vis and photoluminescence spectroscopy, cyclic voltammetry, thermogravimetric analysis (TGA) and DSC. A series of OLEDs including these phosphole derivatives emitting different colors were developed, displaying similar EQEs with DRs varying from 1% to 50%. Furthermore, whiteemission was obtained for DRs varying in quite a large range. These unprecedented properties make these thiophene-phosphole-fluorene derivatives appealing dopants for the tailoring of OLEDs, including WOLEDs that are easy to reproduce.

2. Results and Discussion

2.1. Synthesis

The novel, phosphole-based π -conjugated systems 4a and 4b (Scheme 1) were readily obtained in good yields according to



Scheme 1. Synthetic route to the thioxophosphole-based dopants 5a and 5b. Reactions and conditions: i) Pd(PPh₃)₂Cl₂ (5 mol%) Cul (5 mol%), diisopropylamine, room temperature (RT); ii) 9,9-(dimethyl)-2-bromofluorene, Pd(PPh₃)₂Cl₂ (5 mol%) Cul (5 mol%), di-isopropylamine, tetrahydrofuran (THF), RT; iii) (a) Cp₂ZrCl₂, n-BuLi (2 equiv), THF, -78 °C-RT, 12h; (b) PhPBr₂, THF, -78 °C-RT, 4h; iv) S₈, CH₂Cl₂, RT, 24h.

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Figure 2. Structures and packing of the thio-oxophospholes 5a and 5b in the solid state.

the Fagan-Nugent route^[13] using the mixed diynes 3a and 3b, which were available on a gram scale using Sonogashira coupling.^[14] A terminal methyl group was introduced in **4b** in order to enhance the electrochemical stability of these thienyl-capped derivatives (vide infra). They were transformed into their thioxo derivatives, 5a and 5b, (Scheme 1) to increase their thermal stability, since σ^3 , λ^3 -phospholes are generally not stable enough to undergo vacuum sublimation for device fabrication.^[15] The multinuclear NMR spectra were as expected for unsymmetrical thioxophosphole compounds^[15,16] and the proposed structures were confirmed by mass spectrometry and X-ray diffraction studies (Figure 2). The metric data of these new derivatives are very similar to those of symmetrical phosphole derivatives bearing 2-thienyl or 2-fluorenyl substituents;^[12,16,17] for example. the phosphorus center adopts a distorted tetrahedral geometry with the usual endocyclic P–C bond lengths (5a, 1.814(4) Å; 5b, 1.820(3) Å). For both derivatives, the phosphole and thiophene moieties were almost coplanar (twist angles: 5a, 17.7°; 5b, 1.2°) and the fluorenyl substituents exhibited a large rotational disorder (twist angles: 5a, 56.6°; 5b, 56.0°). It is interesting to compare the packing diagrams of these two related derivatives to probe their ability to aggregate in the solid state. The unit cell of 5a contains 8 molecules, two neighboring molecules being in close contact (3.3–3.6 Å) via intermolecular π - π interactions involving a P-phenyl ring and a fluorene group (Figure 2, right). In addition, a short contact between the H-atom at the

7-position of one fluorene group and the fluorenyl group of a neighboring molecule (2.6 Å) was observed (Figure 2). In the case of **5b**, which features terminal methyl groups (Scheme 1), only 4 molecules are present in the unit cell, indicating a less-congested environment favoring a single-molecule behavior in the solid state (vide infra). The fluorene moieties of two neighboring molecules are π -stacked (π – π distance, 3.6 Å) with a parallel displaced arrangement (Figure 2). These π -dimers are in mutual interaction via CH- π interactions (2.8 Å) involving a P-phenyl H-atom and a fluorenyl moiety (Figure 2, right). The comparison of these packing patterns shows that a tiny molecular variation (Scheme 1: **5a** R = H; **5b**, R = CH₃) has a profound impact on the supramolecular organization of these mixed fluorene-phosphole-thiophene derivatives in the solid state.

2.2. Optical Properties

In order to further establish the structure-property relationship for this novel series of phosphole-based, π -conjugated systems, their UV–vis absorption and fluorescence spectra were measured, both in CH₂Cl₂ and in thin films. In solution, the two phosphole derivatives **5a** and **5b** exhibited an intense band in the UV–visible region, attributed to π – π ^{*} transitions of the extended conjugated system, and broad emissions in the visible region (**Table 1**). The replacement of one of the

Table 1. Optical (solution and in thin films), electrochemical and thermal data for the organophosphorus compounds 5a and 5b, and A.

Compound	λ _m ax ^{a)} [nm]	ε [mol ⁻¹ L cm ⁻¹]	λ em ª) [nm]	${oldsymbol{\Phi}}_{ m f}{}^{ m b)}$ [%]	λ _{em} c) [nm]	$arphi_{ m f}^{ m d)}$ [%]	T _{TGA} ^{e)} [°C]	τ _m f) [°C]	$E_{ox}^{1 g)}$	E ^{2 g)} [V]	$E_{red}^{1 g)}$
A	447	29 320	575	0.5	549	70	-	-	+0.95	+1.28	-1.61
5a	413	13 400	558	5.6	543	54	361	209	+1.24 ^{h)}	+1.41	-1.58
5b	420	14 400	578	0.5	560	55	355	171	+1.13	+1.36	-1.61

^{a)}Measured in CH₂Cl₂; ^{b)}Fluorescence quantum yields determined using fluorescein as standard, ±15%; ^{c)}Dispersed in PMMA (2 wt%); ^{d)}Measured in integrating sphere; ^{e)}Onset weight-loss temperature estimated using TGA under air; ^{f)}Melting point measured by DSC under He; ^{g)}All potentials were obtained during cyclic-voltammetry investigations in 0.2 \bowtie Bu₄NPF₆ in CH₂Cl₂. Platinum-electrode diameter = 1 mm, sweep rate = 200 mV s⁻¹. All of the reported potentials are referenced to a saturated calomel electrode (SCE); ^{h)}Irreversible processes.



methylthiophene substituents on the reference molecule A with a fluorene atom induced a blue shift of the absorption maximum, and the emission maximum was weakly affected $(5b/A; \Delta \lambda_{max} = 27 \text{ nm}, \Delta \lambda_{em} = 3 \text{ nm}, \text{ Table 1})$. Moreover, the introduction of the methyl group $(5a \rightarrow 5b)$ resulted in a slight red-shift of the value of λ_{em} ($\Delta \lambda_{em} = 20$ nm). It is noteworthy that the photoluminescence (PL) quantum yields (QYs) in solution were low and the PL quantum yield of 5a (5.6%) was much higher than that of 5b (0.5%). Since these compounds were being developed as dopants for OLEDs, it was of interest to investigate their PL properties in a poly(methyl methacrylate) (PMMA) matrix. The values of λ_{em} in PMMA (doping rate = 2 wt%) were slightly blue-shifted compared with those recorded in solution (Table 1). Of great interest, the PL QYs of 5a and 5b in a PMMA matrix reached 54-55%, values considerably higher than those observed in solution (Table 1). This behavior, which is very appealing towards the development of the phosphole derivatives, 5a and 5b, as dopants in OLEDs, can be attributed to a rotational restriction in the solid state and to the steric protection provided by the tetrahedral P-center, the endocyclic cylohexane, the bulkiness of the fluorene substituent of complexes 5a and 5b preventing the formation of strong aggregates in the solid state.[12,15]

2.3. Electrochemical Properties

The redox properties of these novel, phosphole-based π -conjugated systems 5a and 5b were determined by cyclic voltammetry (CV), recorded in CH₂Cl₂ using Bu₄NPF₆ as an electrolyte. The nature of the substituents in positions 2 and 5 on the phosphole ring affected the oxidation potentials, while the reduction potentials were not modified (Table 1). For example, the reference molecule A (Figure 1) presents a lower oxidation potential than the fluorene-phosphole-methylthiophene system 5b, which displays a lower oxidation potential than 5a (Table 1).^[12] These data indicate that the lowest-unoccupiedmolecular-orbital (LUMO) level was unchanged and the highest-occupied-molecular-orbital (HOMO) level was gradually stabilized going from compounds A and 5b to 5a. Furthermore, reversible reduction and oxidation processes took place for compound 5b, whereas, for 5a, only the reduction was reversible. It is likely that the presence of the methyl group at the α -position of the S-atom stabilized the thiophene radical cation and also prevented electropolymerization taking place.^[16a,c]

2.4. Thermal Properties

The thermal behaviors of these thiooxophole derivatives **5a** and **5b** were investigated, since a high thermal stability is a key property for device fabrication (sublimation of the organic materials under vacuum) and also for getting a stable device operation. The decomposition temperatures (T_d) established by TGA were above 350 °C (Table 1). This high thermal stability will allow **5a** and **5b** to be used in "small-molecule" OLED technology. The melting points (T_m) were in the range of 170–209 °C (Table 1). The formation of a glassy state of these derivatives after melting and cooling was evidenced ($T_g \approx 80$ °C). Further heating above



the glass-transition temperature resulted in no further crystallization or melting behaviors. These results indicate that these materials present good morphological and thermal stabilities, two critical issues for device stability and lifetime.

2.5. Device Performance/Development of WOLEDs

Since the derivatives **5a** and **5b** are thermally stable and emissive compounds, they could be used as the emitting layer (EML) in the multilayer OLEDs **B**₀ and **C**₀ (**Table 2**), having an indium tin oxide (ITO) (Asahi)/copper phthalocyanine (CuPc) (10 nm)/*N*,*N'*-diphenyl-*N*,*N'*-bis(1-naphthylphenyl)-1,1'-biphenyl-4,4'-diamine (α -NPB) (50 nm)/EML (15 nm)/DPVBi (35 nm)/bathocuproine (BCP) (10 nm)/tris(8-hydroxyquino-linato)aluminium (Alq₃) (10 nm)/LiF (1.2 nm)/Al (100 nm) configuration (**Figure S1**, Supporting Information). The electroluminescence (EL) spectra of devices **B**₀ ($\lambda_{max,EL} = 548$ nm) and **C**₀ ($\lambda_{max,EL} = 572$ nm) resemble the thin-film PL spectra of the thio-oxophosphole derivatives **5a** ($\lambda_{em} = 543$ nm) and **5b** ($\lambda_{em} = 560$ nm) (**Figure S2 and S3**, Supporting Information), respectively, showing that the EL emission bands were from these P-luminophores.

The coevaporation of DPVBi and the phosphole-based dopant 5b was firstly explored in order to construct devices with an ITO (PG&O)/CuPc (10 nm)/a-NPB (50 nm)/doped-DPVBi (50 nm)/ BCP (10 nm)/Alq₃ (10 nm)/LiF (1.2 nm)/Al (100 nm) structure. For a DR of 1%, the EL spectrum consisted of the dual emission of the DPVBi (λ = 460 nm) and of the dopant **5b** (λ = 560 nm) (Figure 3). It is very striking to note that the DPVBi matrix still contributed to the EL spectra of the OLEDs for doping ratios up to 25% (devices C_4 – C_{12} , Figure 3). In fact, the emission of the DPVBi matrix was predominant for DRs between 1% and 3.2% (devices C_4-C_6), and the contribution of the DPVBi emission decreased (devices C_7-C_9) and became weak when the DR level reached 25% (device C_{10} , Figure 3). Moreover, the impact of the DRs on the OLED performances was also very intriguing. The external quantum efficiency (EQE) remained stable $(2.4 \pm 0.1\%)$ for DRs varying between 1% and 50% (Table 2, Figure 4). Note that a "doping rate" of 50% is meaningless, since, in this case, the EML was a 1/1 mixture of two semiconducting electroluminescent derivatives (i.e., DPVBi and 5b). In fact, the EQE recorded for DRs ranging from 1% to 50% was similar to that of the device A_2 , in which the EML was pure DPVBi (Table 2). This very-unusual behavior, which shows that 5b is a quenchresistant dopant, resulted in a very-progressive modification of the device CIE co-ordinates upon increasing the DR (Table 2, devices C_4-C_{12}). The relationship defining the EQE involves the singlet/triplet ratio ($\rho_{S/T}$), the extraction yield ($\eta_{\text{extraction}}$), the recombination rate (β) and the photoluminescent quantum yield ($\eta_{\rm PL}$) of the EML.^[18,6g] For diodes A2 and C4–C11 (Table 2), the first two factors ($ho_{
m S/T}$, $\eta_{
m extraction}$) were constant. Therefore, the fact that the EQE did not vary implies that the recombination rate (β) and the photoluminescence quantum yields (η_{PL}) of the DPBVi/5b EML were either constant or offset each other for DR values ranging from 0% to 50%. PL measurements conducted on DPVBi films doped with 5b revealed that the photoluminescence quantum yield was stable (21%) when the DRs ranged from 1% to 40%.



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Table 2. EL performance of the devices as a function of the device structure and of the doping rate.

Device ^{a)}	EML Doping rate (doping ratio [wt,%])	λ _{max EL} [nm]	V on ^{c)} [V]	V ₂₀ ^{d)} [V]	<i>B</i> ₂₀ ^{d)} [cd m ⁻²]	$\eta_{20}{}^{d)}$ [%]	Power efficiency ^{d)} [lm W ⁻¹]	Current efficiency ^{d)} [cd A ⁻¹]	CIE co-o	rdinates ^{d)}
				ITO Asahi					x	Ŷ
A ₁	DPVBi (<i>0</i>)	448	5.4	10.9	479	2.4	0.7	2.4	0.16	0.13
B ₀ ^{b)}	5a	548	4.7	10.4	705	1.1	1.1	3.3	0.39	0.55
B ₁	DPVBi: 5a (0.3)	448/550	4.7	10.8	832	2.1	1.3	4.3	0.27	0.33
B ₂	DPVBi: 5a (1.4)	552	4.4	10.7	810	1.5	1.2	4.2	0.38	0.51
$\mathbf{C}_{0}^{(b)}$	5b	572	5.9	11.92	509	0.9	0.7	2.5	0.44	0.48
C ₁	DPVBi: 5b (2.1)	464	5.8	11.3	840	2.3	1.2	4.1	0.25	0.30
C ₂	DPVBi: 5b (3.2)	460/556	5.3	12.0	898	2.1	1.3	4.8	0.29	0.35
C ₃	DPVBi: 5b (<i>3.8</i>)	460/552	5.3	11.7	1158	2.5	3.3	5.5	0.31	0.37
	ITO PG&O									
A ₂	DPVBi (<i>0</i>)	460	5.3	11.8	660	2.4	0.9	2.7	0.16	0.20
C ₄	DPVBi: 5b (1)	460	5.6	11.8	968	2.5	1.4	4.9	0.24	0.31
C ₅	DPVBi: 5b (2)	460	5.8	11.8	851	2.3	1.2	4.5	0.26	0.32
C ₆	DPVBi: 5b (3.2)	460/530	5.6	11.5	1061	2.3	1.6	5.4	0.32	0.40
C ₇	DPVBi: 5b (5.3)	464/556	4.9	11.3	1210	2.4	1.7	5.9	0.34	0.43
C ₈	DPVBi: 5b (6)	560	5.0	11.8	1099	2.3	1.2	7.8	0.35	0.44
C ₉	DPVBi: 5b (<i>12</i>)	560	5.0	11.4	1380	2.4	1.8	7.2	0.36	0.48
C ₁₀	DPVBi: 5b (25)	560	4.7	10.8	1035	2.3	2.0	6.2	0.40	0.50
C ₁₁	DPVBi: 5b (50)	564	5.3	11.2	1273	2.3	1.9	6.5	0.42	0.51
C ₁₂	DPVBi: 5b (80)	568	5.4	12.	11.16	1.9	1.6	5.4	0.44	0.51

^{a)}Device configuration (thickness): ITO/CuPc (10 nm)/ α -NPB (50 nm)/doped-DPVBi (50 nm)/BCP (10 nm)/Alq₃ (10 nm)/LiF (1.2 nm)/Al (100 nm); ^{b)}Device configuration (thickness): ITO/CuPc (10 nm)/ α -NPB (50 nm)/EML (15 nm)/DPVBi (35 nm)/BCP (10 nm)/Alq₃ (10 nm)/LiF (1.2 nm)/Al (100 nm) configuration; ^{c)}Turn-on voltage at which emission becomes detectable (0.1 cd m⁻²); ^{d)}Measured at 20 mA cm⁻².

These data therefore suggest that the recombination rate should be constant to account for the stable EQEs observed for the C_4-C_{11} OLEDs. It is difficult to propose a rational explanation to account for this unusual phenomenon, but it seems that the recombination taking place in the DPVBi, the efficient energy transfer between the DPVBi and the dopant and the spatial arrangement of the DPVBi and the dopant **5b** in the doped layer could be responsible. Effectively, a resonant energy transfer between the DPVBi and the absorption spectrum of the DPVBi and the absorption spectrum of the dopant **5b** present some overlap. The calculated Förster

radius (3 nm) (see Supporting Information) was much higher than the spatial separation of the DPVBi and the dopant 5binside the doped layer, leading to a high Förster energy-transfer rate. As a consequence, the energy transfer from DPVBi to 5bwas almost complete. Since the kinetic rate constant for the fluorescence process was high and the energy transfer was almost complete, the photoluminescence quantum yield of the DPVBi films doped with 5b can be expected to be stable for different doping ranges. In order to understand the charge-recombination processes, calculations (at the B2PLYP-D/6-31G(d)//B97-D/6-31G(d) level (see Supporting Information for details)) of



Figure 3. Normalized electroluminescent spectra and CIE chromaticity co-ordinates of devices $C_4 - C_{12}$ (Table 2), recorded at 30 mA cm⁻².



Figure 4. Influence of the doping rate on the external quantum efficiency for devices $C_4 - C_{12}$ and C_0 (Table 2).

the heterodimer (DPVBi-dopant 5b) interaction energy were performed. A few possible potential-energy surface minima for this heterodimer were obtained by optimizing the various initial spatial arrangements of the DPVBi and 5b. The dimer having the largest interaction energy ($\Delta E_{AB} = -26.84 \text{ kcal mol}^{-1}$ (Figure 5)) presented a π - π interaction (3.5 Å), but the π -systems of the DPVBi and 5b didn't overlap strongly, preventing the formation of strong aggregates in the solid state. The frontier molecular orbitals of the dimer (Figure 5) show that the electron density was mostly located on the DPVBi in the HOMO and on the compound 5b in the HOMO-1. Since the difference in energy between the HOMO and the HOMO-1 was small, a hole could be injected to the HOMO levels of each component and be subsequently trapped to the HOMO level of the DPVBi before forming an exciton by recombination with the electron that was mainly located on the DPVBi due to the structure of the OLEDs (Figure S1, Supporting Information). Since the structure (layer thicknesses) of the OLED was not modified, all of these data suggest that the rate of recombination can be constant when the doping rate increases. This behaviour was



Figure 5. Optimized spatial arrangement of DPVBi and **5b**, frontier molecular orbitals of dimer **DPVBi** - **5b** and eigenvalues calculated at B3LYP/6-31G(d,p)//B97-D/6-31G(d) level of theory.



not observed with **5a** because the optical properties, the frontiers orbital and the solid-state arrangement were different to those of the dopant **5b**. Indeed, the derivative **5b** appears to be a unique dopant for DPVBi, due to a combination of electronic and structural properties, making the P-derivatives very attractive from a technical point of view for the development of WOLEDs, since small DR variations had almost no impact, neither on the CIE co-ordinates nor on the EQE.

None of the C_4 - C_{12} OLEDs exhibited a pure-white emission (the best CIE co-ordinates being obtained for DR = 3.2%: device C_6 , Table 2) due to the fact that dopant **5b** did not emit the exact complementary colour of the DPVBi matrix (Figure 3). However, it appears that replacing PG&O ITO with Asahi ITO modified the EL emission of the DPVBi matrix. For the same general device structure (Table 2), the EL spectrum of the diode A_1 (Asahi ITO-coated glass) substrate was blue-shifted ($\Delta \lambda = 12$ nm) compared with that of the A_2 device (PG&O ITO-coated glass). This tiny change is very important, since the derivatives **5a** and **5b** exhibit emission colors that are complementary to that of this novel device A_1 . This modification is likely to be due to a small difference of the ITO thickness inducing a cavity phenomenon.^[19]

The mixed fluorene-phosphole-thiophene derivative 5a was firstly investigated using an Asahi ITO coated glass substrate. The corresponding devices, B_1 and B_2 , exhibited a dual EL emission from DPVBi (448 nm) and the phosphole dopant (550 nm). As classically observed, a small variation of the DR had a large impact, both on the CIE co-ordinates and on the EQE of the devices (Table 2, devices $\mathbf{B}_1/\mathbf{B}_2$).^[12] A well-balanced emission from DPVBi and 5a was obtained for a doping rate of 0.3%, affording the OLED B_1 , which displayed CIE co-ordinates (0.27, 0.33) that are close to pure-white emission. The turn-on voltage of device B_1 was quite low (4.7 V) and it exhibited an EQE of 2.1%, a brightness of 832 cd m^{-2} at 20 mA cm $^{-2}$ and a power efficiency of 1.3 lm W^{-1} (Table 2). These data show that the mixed fluorene-phosphole-thiophene derivative 5a is an efficient dopant for DPVBi towards the development of efficient WOLEDs. However, the required low DR value (approximately

> 0.3%) to reach white emission was guite difficult to control and reproduce within the coevaporation process, since a rather-small variation of the doping rate resulted in an important modification of the device CIE co-ordinates (Table 2). Of great interest, the very-appealing quench properties of dopant 5b, resulting in small variations of the CIE co-ordinates and EQEs upon DR modification, were retained using this novel glass substrate (Asahi ITO). Indeed, the EQE of the C_1 - C_3 OLEDs were almost unchanged $(2.3 \pm 0.2\%)$ for DRs increasing from 2.1% to 3.8% and a WOLED having CIE co-ordinates close to white emission (0.29, 0.35) could be obtained using a DR of 3.2% (device C_2 , Table 2). The performance of this WOLED was very satisfying, with a brightness of 898cdm⁻²at20mAcm⁻² (Table 2). Moreover, the brightness increased regularly with the current density (see Supporting Information),



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showing the good stability of this WOLED, despite the rather high DR. These data show that the mixed fluorene-phospholethiophene derivative **5b** is also an efficient dopant for DPVBi towards the development of efficient WOLEDs. In this case, the DR value (approximately 3.2%) to reach white emission was quite easy to control and reproduce within the coevaporation process since: i) it was rather high, and ii) it could vary without a dramatic modification of the device CIE co-ordinates and the EQE.

3. Conclusions

In conclusion, two phosphole-based dopants **5a** and **5b**, which have very-similar structures (Scheme 1), exhibited very-different doping properties. The doping rate used to reach white emission was much higher with **5b** (3.2%) than with **5a** (0.3%) and, in contrast to what was observed with **5a**, increasing the doping rate ($2.1 \rightarrow 3.8\%$) of **5b** had a small impact on the CIE co-ordinates. Moreover, no modification of the EQE was observed by increasing the doping rate. These two properties make **5b** a very-appealing dopant for the DPVBi matrix towards the development of "easy-to-make" WOLEDs.

4. Experimental Section

General Procedures: All of the experiments were performed under an atmosphere of dry argon using standard Schlenk techniques. The column chromatography was performed in air, unless stated in the text. The solvents were freshly distilled under argon from sodium/benzophenone (tetrahydrofuran (THF), diethyl ether) or from phosphorus pentoxide (pentane, dichloromethane). Bis(cyclopentadienyl)zirconium dichloride (Cp₂ZrCl₂) was obtained from Alfa Aesar Chem. Co. Bis(triphenylphosphine)palladium(II) dichloride (PdCl₂(PPh₃)₂), CuI, 1,7-octadiyne, n-butyl-lithium (n-BuLi), di-isopropylamine and S₈ were obtained from Acros Chem. Co. All of the compounds were used as received without further purification. dibromophenylphosphine (PPhBr₂),^[20] 9,9'-dimethyl-2-bromofluorene^[21] and 2-thienyl-octa-1,7diyne^[16]a] were prepared as described in the literature. Preparative separations were performed by gravity-column chromatography on basic alumina (Aldrich, Type 5016A, 150 mesh, 58 Å) or silica gel (Merck Geduran 60, 0.063-0.200 mm) in 3.5-20 cm columns. ¹H-, ¹³Cand ³¹P-NMR spectra were recorded using a Bruker AM300 or DPX200 instrument. The ¹H- and ¹³C-NMR-spectroscopy chemical shifts are reported in parts per million (ppm), relative to Si(CH₃)₄ as an external standard. The ³¹P-NMR-spectroscopy downfield chemical shifts are expressed with a positive sign, in ppm, relative to external 85% H₃PO₄. The assignment of the proton atoms was based on a correlationspectroscopy (COSY) experiment. The assignment of the carbon atoms was based on heteronuclear-multiple-bond-correlation (HMBC), heteronuclear-multiple-quantum-coherence (HMQC) and distortionlessenhancement-by-polarization-transfer (DEPT-135) experiments. The high-resolution mass spectra were obtained using Varian MAT 311, Waters Q-TOF 2 or ZabSpec TOF Micromass instruments at the Centre Régional de Mesures Physiques de l'Ouest (CRMPO), University of Rennes 1. The elemental analyses were performed by the CRMPO, University of Rennes 1.

Determination of Optical Data: The UV-vis spectra were recorded at room temperature using a UVIKON 942 spectrophotometer and the luminescence spectra were recorded in freshly distilled solvents at room temperature using a PTI spectrofluorimeter (PTI-814 PDS, MD 5020, LPS 220B) with a xenon lamp. The quantum yields were calculated relative to fluorescein ($\Phi = 0.90$ in 0.1 N NaOH).^[22]

Cyclic-Voltammetry Measurements: The electrochemical studies were carried out under argon using an Eco Chemie Autolab PGSTAT 30 potentiostat for cyclic voltammetry with the three-electrode configuration: the working electrode was a platinum disk, the reference electrode was a saturated calomel electrode (SCE), and the counterelectrode was a platinum wire. All of the potentials were internally referenced to the ferrocene/ferrocenium couple. For the measurements, concentrations of 10^{-3} M samples of the electroactive species were used in freshly distilled and degassed dichloromethane (Lichrosolv) (Merck) and 0.2 M tetrabutylammonium hexafluorophosphate (TBAHFP) (Fluka), which was twice recrystallized from ethanol and dried under vacuum prior to use.

Device Fabrication and Characterization: The EL devices, based on a multilayer structure, were fabricated on patterned ITO-coated-glass substrates from Asahi (sheet resistance 10 Ω m⁻¹) or PGO CEC020S (thickness: 100 nm and sheet resistance: less than 20 Ω m⁻¹). The organic materials (from Aldrich and Syntec) were deposited onto the ITO anode by sublimation under high vacuum ($<10^{-6}$ Torr) at a rate of 0.2–0.3 nm s⁻¹. The common structure of all the devices was the following: a thin layer (10 nm thick) of CuPc was used as the hole-injection layer (HIL) and 50 nm of α -NPB was used as the hole-transporting layer (HTL). The emitting layer consisted of a 15 nm-thick film of one of the pure phosphole derivatives or the DPVBi-doped phosphole derivatives. The doped layer was obtained by coevaporation of the two compounds and the doping rate was controlled by tuning the evaporation rate of each material. A thin layer of BCP (10 nm) was used as the hole-blocking layer. Alq₃ (10 nm) was used as electron-transporting layer (ETL). Finally, a cathode consisting of 1.2 nm of LiF capped with 100 nm of Al was deposited onto the organic stack. The entire device was fabricated in the same run without breaking the vacuum. In this study, the thicknesses of the different organic layers were kept constant for all of the devices. The active area of the devices defined by the overlap of the ITO anode and the metallic cathode was 0.3 cm².

The current–voltage–luminance (*I–V–L*) characteristics of the devices were measured using a regulated power supply (Laboratory Power Supply EA-PS 3032-10B) combined with a multimeter and a 1 cm²-area silicon calibrated photodiode (Hamamatsu). The spectral emissions were recorded using a SpectraScan PR650 spectrophotometer. All of the measurements were performed at room temperature and under an ambient atmosphere with no further encapsulation of devices.

Details of the X-Ray Crystallography Study: Single-crystal data collection was performed at 100 K using an APEX II Bruker-AXS (Centre de Diffractométrie, Université de Rennes 1, France) with Mo K radiation (λ = 0.71073 Å). The reflections were indexed, Lorentz polarization corrected and integrated using the DENZO program of the KappaCCD software package. The data-merging process was performed using the SCALEPACK program.^[23] Structure determinations were performed by direct methods using the SIR97 solving program,^[24] which revealed all the non-hydrogen atoms. The SHELXL program (G. M. Sheldrick, SHELX97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997) was used to refine the structures by full-matrix least-squares based on F^2 . All of the non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were included in idealized positions and refined with isotropic displacement parameters. Atomic scattering factors for all of the atoms were taken from International Tables for X-Ray Crystallography. $\ensuremath{^{[25]}}$ Details of the crystal data and structural refinements are provided (Table S2, Supporting Information).

Crystallographic Data: Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-804759 for **5a** and CCDC-804760 for **5b**. Copies of the data can be obtained free of charge from http://www.ccdc.cam. ac.uk/conts/retrieving.html.

Calculations of the Interaction Energy of the Heterodimers: The optimization of the spatial arrangements of the DPVBi and **5b** was carried out using Grimme's specially designed semilocal density functional augmented with dispersion corrections (B97-D), especially

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recommended for van der Waals complexes.^[26] Due to the large size of the system, we used only a moderate Pople's split valence 6-31G(d) basis set. The interaction (association) energy, ΔE , was obtained from a single-point calculation using the dispersion-corrected double-hybrid functional, B2PLYP-D, and a moderate basis set, 6-31G(d,p), using B97-D/6-31G(d) minimized structures,^[26] by Equation 1:

$$\Delta E_{AB} = E_{AB} - E_A - E_B \tag{1}$$

In Equation 1, E_{AB} is the total energy of the optimized dimer and E_A and E_B are the single-point energies of the isolated monomers A and B extracted from the optimized dimer. The HOMO and LUMO orbital energies were estimated at the B3LYP/6-31G(d,p) level using the B97-D/6-31G(d) optimized geometries. All of the computations were done using G09 software.^[27]

Synthesis of 1-(5-Methyl-2-thienyl)octa-1, 7-diyne (2b): Catalytic amounts of [PdCl₂(PPh₃)₂] (104 mg, 0.37 mmol) and CuI (28 mg, 0.37 mmol) were added to a solution of octa-1,7-diyne (1.6 ml, 12 mmol) and 2-methyl-5-iodothiophene (0.9 ml, 7.4 mmol) in di-isopropylamine (25 ml). The heterogeneous, brown mixture was stirred overnight at room temperature. All volatile materials were removed in vacuo and the residue was extracted using diethyl ether $(3 \times 20 \text{ ml})$. After purification by column chromatography on silica gel (n-heptane/ethyl acetate, 95:5, v:v, $R_{\rm f}=$ 0.64) and by vacuum distillation, the product was obtained as a yellow oil (yield 30%, 450 mg, 2.22 mmol). ¹H NMR (300 MHz, CDCl₃, δ): 6.93 (d, 3J(H,H) = 3.6 Hz, 1H, $H_{thienyl}$), 6.59 (dd, 3J(H,H) = 3.6 Hz, 4J(H,H) = 0.9 Hz, 1H, H_{thienyl}), 2.43 (m, 5H, CH₂C=C_{thienyl} and CH₃), 2.26 (m, 2H, $CH_2C=CH$), 1.98 (t, 3J(H,H) = 2.7 Hz, 1H, C=CH), 1.71 (m, 4H, CH₂); ¹³C NMR (75 MHz, CDCl₃, δ): = 140.6 (s, CH_{thienyl}), 131.2 (s, CH_{thienyl}), 125.0 (s, CH_{thienyl}), 121.6 (s, C_{thienyl}), 92.8 (s, CH₂C=C_{thienyl}), 84.1 (s, CH₂C=CH), 74.4 (s, CH₂C=C_{thienyl}), 68.6 (s, C=CH), 27.6 (s, CH₂), 19.2 (s, CH₂C=CH), 18.0 (s, CH₂C=C_{thienvl}), 15.3 (s, CH₃); HRMS (EI, m/z): $[M + Na]^+$ calcd for $C_{13}H_{14}S$, 225.07139; found, 225.0717. Anal. Calcd for C₁₃H₁₄S: C 77.18, H 6.97, S 15.85; found: C 77.69, H 7.21, S 14.64.

Synthesis of 1-(2-Thienyl)-8-(9,9'-dimethylfluoren-2-yl)-1,7-octadiyne (3a): Catalytic amounts of [PdCl₂(PPh₃)₂] (101 mg, 0.14 mmol) and Cul (27 mg, 0.14 mmol) were added to a solution of 1-(2-thienyl)octa-1,7-diyne (545 mg, 2.9 mmol) and 9,9'-dimethyl-2-bromofluorene (799 mg, 2.9 mmol) in THF (30 ml) and di-isopropylamine (30 ml). The heterogeneous, brown mixture was stirred for 1 d at 55 °C. All volatile materials were removed in vacuo and the residue was extracted using diethyl ether (3 \times 20 ml). After purification by column chromatography on silica gel (heptane, $R_f = 0.2$), the product was obtained as a yellow oil (yield 77%, 852 mg, 2.2 mmol). ¹H NMR (300 MHz, CDCl₃, δ): 7.77 (m, 1H, H_{fluorenyl}), 7.72 (d, 3J(H,H) = 7.8 Hz, 1H, H_{fluorenyl}), 7.62 (s, 1H, H_{fluorenyl}), 7.54–7.49 (m, 2H, H_{fluorenyl}), 7.44–7.39 (m, 2H, H_{fluorenyl}), 7.24 (d, 3J(H,H) = 5.1 Hz, 1H, $H_{thienyl}$), 7.23 (dd, 3J(H,H) = 3.6 Hz, $4J(H,H) = 1.2 Hz, 1H, H_{thienyl}, 7.00 (dd, 3J(H,H) = 3.6 Hz, 3J(H,H) =$ 5.1 Hz, 1H, H_{thienvl}), 2.61 (m, 4H, C≡CCH₂), 1.91 (m, 4H, CH₂), 1.58 (s, 6H, CH₃); ¹³C-{¹H} NMR (75 MHz, CDCl₃, δ): 153.9 (s, C_{fluorenyl}), 153.6 (s, $C_{fluorenyl}$), 138.8 (s, $C_{fluorenyl}$), 138.7 (s, $C_{fluorenyl}$), 131.1 (s, $CH_{thienyl}$), 130.8 (s, $CH_{fluorenyl}$), 127.6 (s, $CH_{fluorenyl}$), 127.2 (s, $CH_{fluorenyl}$), 126.9 (s, CH_{thienyl}), 126.0 (s, C_{thienyl}), 125.9 (s, CH_{fluorenyl}), 124.3 (s, C_{thienyl}), 122.7 (s, CH_{fluorenyl}), 122.6 (s, C_{fluorenyl}), 120.3 (s, CH_{fluorenyl}), 119.9 (s, CH_{fluorenyl}), 94.0 (s, C≡C-C_{thienyl}), 89.8 (s, C≡C-C_{fluorenyl}), 81.9 (s, C≡C-C_{fluorenyl}), 74.3 (s, C≡C-C_{thienyl}), 46.8 (s, C_{flurorenyl}), 28.1 (s, C≡CCH₂), 27.9 (s, C≡CCH₂), 27.1 (s, CH3fluorenyl), 19.4 (s, CH2), 19.2 (s, CH2). HRMS (ESI, m/z): [M.]+ calcd for C₂₇H₂₄S, 380.45987; found, 380.1614. Anal. calcd for C₂₇H₂₄S: C 85.22, H 6.36, S 8.43; found: C 85.66, H 6.50, S 8.38.

Synthesis of 1-(5-Methyl-2-thienyl)-8-(9,9'-dimethylfluoren-2-yl)-1,7-octadiyne (**3b**): Catalytic amounts of $[PdCl_2(PPh_3)_2]$ (20 mg, 0.03 mmol) and CuI (5 mg, 0.03 mmol) were added to a solution of 1-(2-methylthiophene)octa-1,7-diyne (292 mg, 1.4 mmol) and 9,9'-dimethyl-2-bromofluorene (414 mg, 1.5 mmol) in THF (20 ml) and di-isopropylamine (5 ml). The heterogeneous, brown mixture was stirred for 1 d at 55 °C. All volatile materials were removed in vacuo and the residue was extracted with diethyl ether (3 × 20 ml). After purification by column chromatography on silica gel (heptane/ethyl acetate, 95/5 v/v,



 $\begin{array}{l} R_{\rm f} = 0.4) \mbox{ the product was obtained as a yellow oil (yield 26%, 146 mg, 0.36 mmol). ¹H NMR (300 MHz, CDCl₃, <math>\delta$): 7.72 (m, 1H, $H_{fluorenyl}$) 7.66 (d, $3J({\rm H},{\rm H}) = 7.8$ Hz, 1H, $H_{fluorenyl}$), 7.49 (s, 1H, $H_{fluorenyl}$), 7.46–7.39 (m, 2H, $H_{fluorenyl}$), 7.37–7.32 (m, 2H, $H_{fluorenyl}$), 6.77 (AB system, $3J({\rm H},{\rm H}) = 3.0$ Hz, $\Delta \upsilon = 104.5$ Hz, 2H, $H_{fluorenyl}$), 6.77 (AB system, $3J({\rm H},{\rm H}) = 3.0$ Hz, $\Delta \upsilon = 104.5$ Hz, 2H, $H_{fluorenyl}$), 5.24 (m, 4H, CH₂-C=C), 2.47 (s, 3H, CH_{3thienyl}), 1.84 (m, 4H, CH₂), 1.51 (s, 6H, CH_{3fluorenyl}); 1³C NMR (75 MHz, CDCl₃, δ): 153.8 (s, $C_{fluorenyl}$), 153.5 (s, $C_{fluorenyl}$), 140.6 (s, $C_{thienyl}$), 138.8 (s, $C_{fluorenyl}$), 127.1 (s, CH_{fluorenyl}), 125.9 (s, CH_{fluorenyl}), 126.0 (s, CH_{fluorenyl}), 122.6 (s, CH_{fluorenyl}), 122.5 (s, Cf_{luorenyl}), 121.7 (s, $C_{thienyl}$), 120.2 (s, CH_{fluorenyl}), 119.8 (s, CH_{fluorenyl}), 74.4 (s, C=C-Cthienyl), 88.8 (s, C=C-Cthienyl), 81.7 (s, C=C-Cthuorenyl), 74.4 (s, C=C-Cthienyl), 19.4 (s, CH₂), 19.1 (s, CH₂), 15.3 (s, CH_{3thienyl}); FMMS (ESI, m/z): [M + Na]⁺ calcd for C₂₈H₂₆SNa, 417.16529; found, 417.1653. Anal. calcd for C₂₈H₂₆S: C 85.23, H 6.64, S 8.13; found: C 83.62, H 6.89, S 8.45. \\ \end{array}

of 1-Phenyl-2-(9,9'-dimethylfluoren-2-yl)-5-(2-thienyl)thio-Synthesis oxophosphole (5a): A hexane solution of n-BuLi (2.5 m, 0.8 ml, 2.05 mmol) was added dropwise (approximately 1 min) at -78 °C to a THF solution (10 ml) of Cp₂ZrCl₂ (286 mg, 1.00 mmol) and 1-(9,9'-dimethylfluoren-2-yl)-8-(2-thienyl)-1,7-octadiyne 3a (366 mg, 1.00 mmol). The solution was warmed to room temperature and stirred overnight. Freshly distilled PhPBr₂ (0.22 ml, 1.05 mmol) at -78 °C was added to this solution. The solution was allowed to warm to room temperature and stirred for 30 h. The solution was filtered on basic alumina (THF) and any volatile materials were removed in vacuo. The yellow precipitate containing the phosphole 4a (³¹P–{¹H} NMR (80 MHz, CDCl₃): δ = 11.3) was dissolved in CH₂Cl₂ (20 ml) and elemental sulfur (32 mg, 0.12 mmol) was added to this solution. The solution was stirred for 4 d at room temperature and chromatographed on silica gel (eluent n-heptane/ethyl acetate, 8/2 v/v, $R_f = 0.5$). 5a was obtained as a yellow-orange solid (yield = 70%, 0.7 mmol, 364 mg). $T_{TGA,10\%} = 376^{\circ}C$; ¹H NMR (300 MHz, CDCl₃, δ): 7.90 (dd, 4J(H,H) = 1.6 Hz, 3J(H,H) = 7.1 Hz, 3J(P,H) = 13.8 Hz, 2H, H_{ortho}), 7.67 (m, 1H, $H_{fluorenyl}$), 7.62 (d, 3J(H,H) = 7.9 Hz, 1 H, $H_{fluorenyl}$), 7.55–7.40 (m, 7 H, 2 H_{fluorenyl}, 2 H_{thienyl}, 2 H_{meta}, H_{para}), 7.34 (m, 2H, $H_{fluorenyl}$), 7.29 (d, 3J(H,H) = 8.0 Hz, 1 H, $H_{fluorenyl}$), 7.05 (dd, 3J(H,H) = 3.8 Hz, 3J(H,H) = 5.1 Hz, 1H, $H_{thienyl}$, 3.04 (s, 4H, C=CCH₂), 2.88 (s, 4H, C=CCH₂), 1.97 (m, 4H, CH₂), 1.81 (m, 4H, CH₂), 1.42 (s, 6H, CH₃). ¹³C NMR (50 MHz, CDCl₃, δ): 153.9 (s, C_{fluorenyl}) 153.5 (s, C_{fluorenyl}), 148.5 (d, ²J(P,C) = 22.0 Hz, C_{β}), 145.2 (d, ²J(P,C) = 22.3 Hz, C_{β}), 138.8 (s, $C_{fluorenyl}$), 138.6 (s, $C_{fluorenyl}$), 135.1 (d, ²] (P,C) = 17.1 Hz, $C_{thienyl}$), 135.2 $(d, {}^{1})(P,C) = 81.7 \text{ Hz}, C_{ipso}), 131.9 (d, {}^{4})(P,C) = 3.0 \text{ Hz}, CH_{para}), 131.4$ $(d, {}^{2}J(P,C) = 22.0 \text{ Hz}, CH_{fluorenyl}), 130.6 (d, {}^{3}J(P,C) = 11.5 \text{ Hz}, CH_{orhto}),$ 129.1 (d, ¹J(P,C) = 73.1 Hz, C_{α}), 128.8 (d, ³J(P,C) = 12.3 Hz, CH_{meta}), 128 (d, ${}^{3}J(P,C) = 5.8$ Hz, $CH_{fluorenyl}$), 127.8 (d, ${}^{2}J(P,C) = 5.3$ Hz, $CH_{thienyl}$), 127.5 (s, CH_{fluorenyl}), 127.2 (s, CH_{thienyl}), 127.0 (s, CH_{fluorenyl}), 126.8 (s, $CH_{thienyl}$, 123.4 (d, ²J(P,C) = 5.5 Hz, $CH_{fluorenyl}$), 122.6 (s, $CH_{fluorenyl}$), 120.1 (s, CH_{fluorenyl}), 119.7 (s, CH_{fluorenyl}), 46.7 (s, C_{fluorenyl}), 28.9 (d, ³J(P,C) = 13.2 Hz, C=CCH₂), 28.8 (d, ³J(P,C) = 13.2 Hz, C=CCH₂), 26.8 (s, CH₃), 26.7 (s, CH₃), 22.7 (s, CH₂), 22.6 (s, CH₂); ³¹P-{¹H} NMR (121.5 MHz, CDCl₃, δ): 53.0 (s). HRMS (ESI, m/z): [M + Na]⁺ calcd for C₃₃H₂₉PS₂Na, 543.1346; found, 543.1343; [M + H]⁺ calcd for C₃₃H₃₀PS₂, 521.152658; found, 521.1525. Anal. calcd for C₃₃H₂₉PS₂: C 76.12, H 5.61, S 12.32; found: C 76.66, H 5.78, S 12.56.

1-Phenyl-2-(9,9'-dimethylfluoren-2-yl)-5-(5-methyl-2-Svnthesis of thienyl)thio-oxophosphole (5b): A hexane solution of n-BuLi (2.5 m, 0.8 ml, 2.05 mmol) was added dropwise (approximately 1 min) at -78 °C to a THF solution (10 ml) of Cp₂ZrCl₂ (286 mg, 1.00 mmol) and 1-(9,9'-dimethylfluoren-2-yl)-8-(5-methyl-2-thienyl)-1,7-octadiyne 3b (395 mg, 1.00 mmol). The solution was warmed to room temperature and stirred over night. Freshly distilled PhPBr₂ (0.22 ml, 1.05 mmol)was added to this solution at -78 °C. The solution was allowed to warm to room temperature and was stirred for 30 h. The solution was filtered on basic alumina (THF) and the volatile materials were removed under vacuum. The yellow precipitate containing the phosphole **4b** $({}^{31}P-{}^{1}H)$ NMR (80 MHz, CDCl₃): $\delta = 13.0$) was dissolved in CH₂Cl₂ (20 ml) and elemental sulfur (32 mg, 0.12 mmol) was added to this solution. The solution was stirred for 1 d at room temperature and chromatographed



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on silica gel (eluent: heptane/ethyl acetate, 95/5 v/v, $R_f = 0.4$). 5b was obtained as a yellow-orange solid (yield = 70%, 0.7 mmol, 374 mg). $T_{\text{TGA,10\%}} = 365 \text{ °C; }^{1}\text{H NMR} (300 \text{ MHz, } \text{CD}_{2}\text{Cl}_{2}, \delta): 7.74 \text{ (ddd, } 4J(\text{H},\text{H}))$ = 1.5 Hz, 3J(H,H) = 6.9 Hz, 3J(P,H) = 13.8 Hz, 2H, H_{ortho}), 7.58 (m, 1H, $H_{fluorenyl}$), 7.51 (d, 3J(H,H) = 7.8 Hz, 1H, $H_{fluorenyl}$), 7.41–7.31 (m, 4H, 2 H_{meta}, H_{para}, H_{fluorenyl}) 7.28 (s, 1H, H_{fluorenyl}) 7.23-7.20 (m, 2H, H_{fluorenyl}), 7.16 (d, J(H,H) = 7.8 Hz, 1H, H_{fluorenvl}) 7.08 (AB system, 3J(H,H) = 3.6 Hz, $\Delta v = 150.1$ Hz, 2H, $H_{thienyl}$), 2.87 (m, 2H, C=CCH₂), 2.74 (m, 2H, C=CCH₂), 2.38 (s, 3H, CH_{3thienyl}), 1.64 (m, 4H, CH₂), 1.29 (s, 6H, CH_{3fluorenvl}); ¹³C NMR (75 MHz, CD₂Cl₂, δ): 154.3 (s, C_{fluorenvl}), 153.9 (s, $C_{fluorenvl}$, 148.9 (d, 2J(P,C) = 22.1 Hz, C_{β}), 143.9 (d, 2J(P,C) = 22.4 Hz, C_{β}), 142.5 (s, C_{thienyl}), 139.1 (s, C_{fluorenyl}), 139.0 (s, C_{fluorenyl}), 133.4 (d, 1J(P,C) $= 82.0 \text{ Hz}, C_{ipso}), 133.3 \text{ (d, } 2J(P,C) = 17.1 \text{ Hz}, C_{thienyl}), 132.2 \text{ (d, } 4J(P,C) = 17.1 \text{ Hz}, C_{t$ 2.9 Hz, CH_{para}), 131.8 (d, 2J(P,C) = 12.3 Hz, C_{fluorenyl}), 130.9 (d, 2J(P,C) = 11.5 Hz, CH_{ortho}), 130.1 (d, 1J(P,C) = 72.0 Hz, C_{α}), 129.1 (d, 3J(P,C)= 12.3 Hz, CH_{meta}), 129.0 (d, 1J(P,C) = 81.7 Hz, C_{α}), 128.6 (d, 4J(P,C)= 5.7 Hz, $CH_{thienvl}$), 128.4 (d, 3/(P,C) = 5.8 Hz, $CH_{fluorenvl}$), 127.8 (s, CH_{fluorenyl}), 127.4 (s, CH_{fluorenyl}), 126.0 (s, CH_{thienyl}), 123.7 (d, 3J(P,C) = 5.5 Hz, CH_{fluorenyl}), 123.0 (s, CH_{fluorenyl}), 120.4 (s, CH_{fluorenyl}), 120.0 (s, CH_{fluorenyl}), 47.1 (s, CH_{3fluorenyl}), 29.3 (s, C=CCH₂), 29.1 (s, C=CCH₂), 27.2 (s, CH_{3fluorenyl}), 27.1 (s, CH_{3fluorenyl}), 23.2 (s, CH₂), 23.0 (s, CH₂), 15.4 (s, CH_{3thienyl}); ³¹P NMR (121 MHz, CD₂Cl₂, δ): 52.5 (s); HRMS (ESI, *m/z*): $[M + H]^+$ calcd for C₃₄H₃₂PS₂, 535.16831; found, 535.1701. Anal. calcd for C₃₄H₃₁PS₂: C 76.37, H 5.84, S 11.99; found: C 76.28, H 6.02, S 12.05.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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