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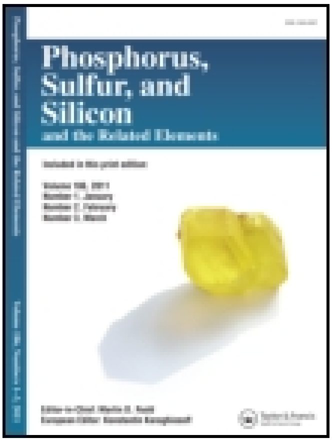

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Phosphorus-Based Chromophores: Emitters for OLEDs

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PHOSPHORUS-BASED CHROMOPHORES: EMITTERS FOR OLEDS

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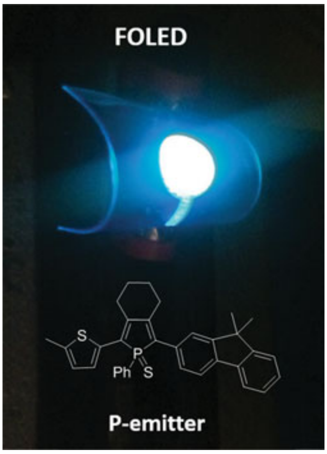
GRAPHICAL ABSTRACT



Abstract *In this paper, we present the development of white OLEDs (WOLEDs) using organophosphorus derivatives as fluorescent emitters. The structural changes that we have performed on and around the phosphole ring (functionalization of the phosphorus atom, nature of the substituents at the 2 and 5 position) allow the ability to tune the emission wavelengths and the color emitted by the OLEDs. Using this concept, we developed organophosphorus dopants emitting orange light, which can be mixed with a blue-emitting matrix for the development of WOLEDs. The OLEDs structure allows the development of flexible OLEDs with good performance and CIE coordinates which are independent from the current density.*

Keywords Phosphole; π-conjugated systems; WOLEDs; optoelectronics

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INTRODUCTION

The development of technologies based on molecular electronics (field-effect transistors (OFET), light-emitting diodes (OLED), solar cells . . .) was accompanied by a strong development of the synthesis and photophysical studies of organic and organometallic compounds having an extended π-conjugated system.[1] Indeed, the development of efficient "plastic electronic" devices is only possible with control of electronic properties and macroscopic organization of these active compounds. A great deal of attention has, therefore, been focused on tuning the structure of the organic π-conjugated materials in order to control their electronic nature (band gap, HOMO and LUMO levels, effective conjugation length, etc.) in such a way that it suits the desired function (electroluminescence, high-charge mobility, etc.). In this perspective, oligomers and π-linear conjugated polymers incorporating heteroatoms have received special attention.[1,2] The incorporation of heterocyclopentadienes (thiophene, pyrrole, silole . . .) allows the emergence of new geometric and electronic properties directly related to the nature of the heteroelement.[3] In this context, the phosphole ring is an attractive synthon because it displays electronic properties that are markedly different from those of the widely used highly aromatic thiophene and pyrrole rings.[4] The key property of the phosphole ring for the molecular engineering of π-conjugated systems is the presence of a reactive phosphorus center due to the low aromatic character of this P-heterole. In fact, delocalization within the phosphole ring arises from a hyperconjugation involving the exocyclic P-R σ-bond and the π-system of the dienic moiety leading to σ-π hyperconjugation phenomenon.[4] The insertion of this P-heterocycle within classical π-conjugated systems results in a lowering of their HOMO-LUMO gaps[5c-e] because conjugation is enhanced for macromolecules incorporating units exhibiting low resonance energies. Moreover, the phosphole building block is a potential source of further structural variations by (1) changing the nature of the P-substituent, (2) chemical modifications of the nucleophilic P-atom, (3) using this P-ring as a precursor to other P-heterocycles featuring a π-system such as phosphametallocenes, or (4) inserting the phosphole into a 2D graphenic scaffold (Figure 1).[6] These properties indicate that the phosphole is a good candidate for the construction of tuneable emissive π-conjugated systems.

RESULT AND DISCUSSION

The introduction of phosphole building blocks in π-conjugated systems allows the ability to perform molecular engineering of these π-systems using the power of phosphorus chemistry. Simple chemical modifications performed on the phosphorus atom (oxidation, coordination chemistry . . .) allows straightforward access to a wide range of novel π-conjugated systems with diverse optical and electrochemical properties, without the need for additional multistep syntheses.[5c,d,6] This strategy allowed us to optimize the emission properties of the organophosphorus chromophores for the development of electroluminescent diodes emitting different colors (yellow, orange . . .).[6a-c,h] The performances of these diodes are notable for fluorescent compounds. Following this work, we decided to use our expertise to develop a novel series of orange-emitting dopants incorporating a phosphole ring for the development of white OLEDs (WOLEDs). The use of the Fagan-Nugent conditions on the dialkynes **1a,b** to generate the phosphole, followed by oxidation with S_8 afforded thioxophospholes **2a,b** (Scheme 1).[5c] These air stable compounds display ^{31}P NMR chemical shifts in the usual range of thioxophopholes (**2a**: +51.6, **2b**: +52.5 ppm) and all their ^{1}H and ^{13}C NMR spectroscopic data support the proposed structures.

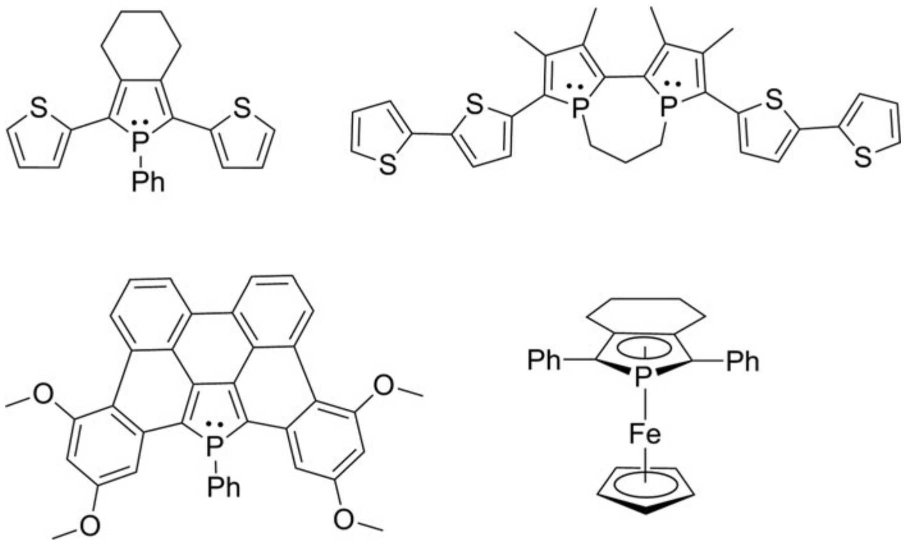


Figure 1 Example of phosphole-based π-conjugated systems.

Optical properties of **2a**,**b** were studied in CH_2Cl_2 and in thin films by means of UV-vis absorption and fluorescence (Table 1). The two compounds show broad absorption in the visible range (Table 1), attributed to $\pi-\pi^*$ transitions of the extended conjugated system, and a broad emission in the orange region of the visible spectrum. The replacement of the methylthiophene substituent by a fluorenyl group does not dramatically modify the physical properties. The maximum of absorption is blue shifted, the emission is weakly affected (**2b**/**2a**; $\Delta\lambda_{max} = 27$ nm, $\Delta\ \lambda_{em} = 3$ nm, Table 1) and the photoluminescence (PL) quantum yields (QYs) in solution are low. It was of interest to investigate their PL property in a polymethylmethacrylate (PMMA) matrix because these compounds are used as solid state emitters in OLEDs. The maxima of emission in PMMA (doping rate, 2 wt.%) are only slightly blue-shifted compared to those recorded in solution (Table 1) and the PL QYs of **2a**,**b** in PMMA matrix reach 55%–70%, values that are considerably higher than those observed in solution (Table 1). These observations, which are very appealing toward the development of phosphole derivatives **2a**,**b** as emitters for OLEDs, can be attributed to

Table 1 Optical (solution and in thin films) and electrochemical properties for the organophosphorus compounds **2a**,**b**

Compound	$\lambda_{max}{}^{a}$ (nm)	ε (mol^{-1}.L. cm^{-1})	$\lambda_{em}{}^{a}$ (nm)	$\Phi_f{}^{b}$ (%)	$\lambda_{em}{}^{c}$ (nm])	$\varphi_f{}^{d}$ (%)	$E^{1}_{ox}{}^{e}$ (V)	$E^{2}_{ox}{}^{e}$ (V)	$E^{1}_{red}{}^{e}$ (V)
2a	447	29320	575	0.5	549	70	+0.95	+1.28	−1.61
2b	420	14400	578	0.5	560	55	+1.13	+1.36	−1.61

[a] Measured in CH_2Cl_2;

[b] fluorescence quantum yields determined using fluorescein as standard, ±15%;

[c] dispersed in PMMA (2 wt.%.);

[d] measured in an integrating sphere;

[e] all potentials were obtained during cyclic voltammetric investigations in 0.2 M Bu_4NPF_6 in CH_2Cl_2. Platinum electrode diameter 1 mm, sweep rate: 200 mV s^{-1}. All reported potentials are referenced to SCE.

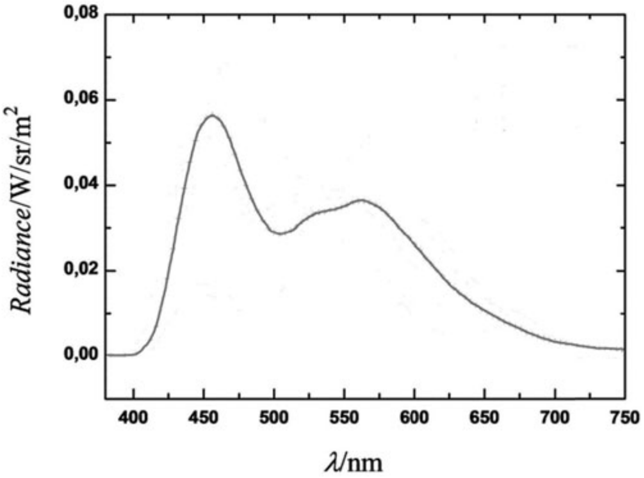


Figure 2 EL spectra of the device **A** recorded at 30 mA/cm^2.

rotational restriction in the solid state and to steric protection provided by the tetrahedral P-center, the endocyclic cyclohexane, and the bulkiness of the fluorene and methylthiophene substituent of compounds **2a,b** preventing the formation of organized stacks in the solid state.[6c,h]

The redox properties of these novel phosphole-based π-conjugated systems **2a**,**b** were determined by cyclic voltammetry (CV) recorded in CH_2Cl_2 using Bu_4NPF_6 as the electrolyte. The compounds **2a**,**b** present reversible reduction and oxidation processes. Furthermore, the nature of the substituents in position 2 and 5 on the phosphole ring affects the oxidation potentials while the reduction potentials are not modified (Table 1). The LUMO level is unchanged and the HOMO level is stabilized going from compound **2a** to **2b** because molecule **2a** (Scheme 1) presents a lower oxidation potential than compound **2b** (Table 1).

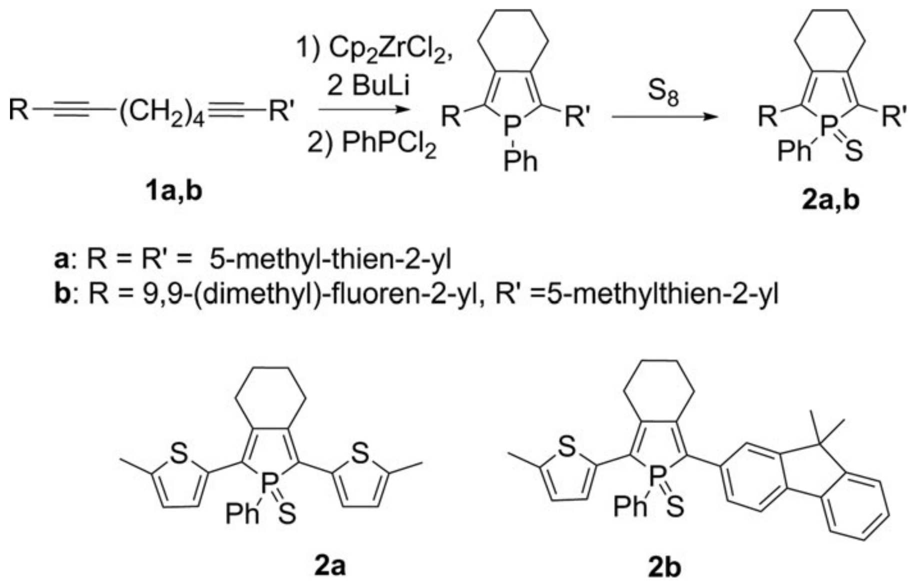
Since compounds **2a**,**b** are redox and thermally stable up to 300°C and present an orange emission (Table 1), we decided to coevaporate them with a blue emitter, 4,4'-bis(2,2'-diphenylvinyl)biphenyl (DPVBi) for the construction of the active layer in WOLEDs. Effectively, white emission could potentially be obtained by combining orange and blue emissions if the ratio of the two colours is correct.[7] First, we developed a multilayer WOLED on a glass substrate having an (ITO/CuPc (10 nm)/α-NPB (50 nm)/doped-DPVBi (50 nm)/Alq_3 (10 nm)/LiF (1.2 nm)/Al (100 nm) structure. Doping of the blue matrix with 0.2% of compound **2a** lead to an OLED exhibiting a small turn-on voltage (5.2 V) with current and power efficiencies of 7.0 cd A^{-1} and 2.3 lm/W, respectively. Its electroluminescent spectrum presents well-balanced emission characteristics of the DPVBi (452 nm, FWHM = 70 nm) and of the dopant **2a** (548 nm, FWHM = 115 nm) (Figure 2). The resulting CIE coordinates of device **A** (0.31;0.39) are close to those of pure white light (0.33,0.33) (Table 2) and are independent of the driving current. These data show that phosphole-based small molecules can be used as dopants for DPVBi toward the development of efficient WOLEDs. However, the required low doping rate value (*ca.* 0.2%) to reach white emission is quite difficult to control and to reproduce within the coevaporation process.

In order to circumvent this problem, thioxophosphole **2b** (Scheme 1) was then studied as the dopant for the DPVBi matrix because this compound possesses a weak ability to

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

Device	Doped layer; dopant[a] Doping rate [wt. %]	λ_{max}^{EL} (nm)	Turn-on voltage[c] (V)	External quantum efficiency (%)	Current efficiency (cd A^{-1})	Power efficiency (lm W^{-1})	CIE coordinates (x,y)
A	DPVBi:**2a**(0.2%)	444/548	5.2	2.7	7.0	2.3	(0.31, 0.39)
B	DPVBi:**2b**(3.8%)	460/552	5.3	2.5	5.5	3.3	(0.31, 0.37)
C	DPVBi:**2b**(1.4%)	460/540	4.6	2.8	7.0	2.4	(0.20, 0.30)
D	DPVBi:**2b**(1.4%)[b]	460/530	4.8	2.3	6.3	1.9	(0.18, 0.25)

[a] Device configurations (thickness): glass/ITO/CuPc (10 nm)/α-NPB (50 nm)/doped-DPVBi (50 nm)/Alq_3 (10 nm)/LiF (1.2 nm)/Al (100 nm);
[b] device configurations (thickness): PET/ITO/CuPc (10 nm)/α-NPB (50 nm)/doped-DPVBi (50 nm)/Alq_3 (10 nm)/LiF (1.2 nm)/Al (100 nm);
[c] turn-on voltage at which emission becomes detectable ($\sim 10^{-2}$ cd.m^{-2}).



a: R = R' = 5-methyl-thien-2-yl
b: R = 9,9-(dimethyl)-fluoren-2-yl, R' =5-methylthien-2-yl

Scheme 1 Synthetic routes to phosphole-based dopants.

aggregate in the solid state.[6c] Effectively, a doping rate of 3.8% was necessary to obtain CIE coordinates that are close to white emission (0.31, 0.37). The performance (Table 2) of this WOLED is very satisfying with a brightness of 1158 cd.m^{-2} at 20 mA/cm^2. Moreover, the brightness regularly increases with the current density showing the good stability of this WOLED in spite of the rather high doping rate. In this case, the doping rate value to reach white emission is quite easy to control and to reproduce within the coevaporation process compared to the first case. Furthermore, a decrease of the doping rate (1.4%, Table 2) has an effect on the CIE coordinates (0.20, 0.30) but the efficiencies are not modified. The device **C** emits a bluish white emission (brightness of 3770 cd.m^{-2} at 20 mA/cm^2) because the contribution of the emission of DPVBi in the electroluminescence spectrum is increased.

This interesting result prompted us to develop flexible OLEDs because these devices can be used in completely new lighting designs.[8] We kept the structure of the device **C** but we changed the glass substrate to poly(ethylene terephthalate) (PET) substrate. The performances of the device **D** are very similar to device **C**. The flexible device **D** exhibits a small turn-on voltage (4.8 V) with current and power efficiencies of 6.3 cd A^{-1} and 1.9 lm/W, respectively. The CIE coordinates, which are similar to device **C,** are independent of the driving current. The performance (Table 2) of this flexible device **D** is very satisfying with a brightness of 2915 cd.m^{-2} at 20 mA/cm^2. All these results demonstrate that phosphole-based emitters can be used for the development of efficient fluorescent OLEDs.

CONCLUSION

These results show the significant potential of phospholes for applications in optoelectronics and namely for the construction of WOLEDs. The major advantage of the phosphole ring relative to other more traditional heterocyclopentadienes (thiophene, pyrrole) is the presence of a reactive heteroatom. Thus, from a single organophosphorus compound, it is possible to prepare easily a family of new chromophores presenting very different optical and redox properties. In addition, the possibility of achieving coordination chemistry opens up broad prospects including the development of diodes using phosphorescence or the development of biosensors.

EXPERIMENTAL

Device Fabrication and Characterization: EL devices, based on a multilayer structure have been fabricated onto patterned ITO-coated glass substrates from Xin Yan Technology (sheet resistance 20 Ω/sqr) or ITO coated on PET substrate from Sigma-Aldrich. The organic materials (from Lumtec) are deposited onto the ITO anode by sublimation under high vacuum ($<10^{-6}$ Torr) at a rate of 0.2–0.3 nm/s. The common structure of all the devices is the following: a thin layer (10-nm thick) of copper phtalocyanine (CuPc) is used as hole injection layer (HIL) and 50 nm of *N*,*N*'-diphenyl-*N*,*N*'-bis(1-naphthylphenyl)-1,1'-biphenyl-4,4'-diamine (α-NPB) as hole transporting layer (HTL). The emitting layer consists of phosphole derivatives (15 nm). A thin layer of 4,4'-bis(2,2'-diphenylvinyl)biphenyl (DPVBi) (35 nm), a commercially available molecule (from Syntec) is used as electron transporting layer (ETL). A thin layer of bathocuproine (BCP) (10 nm) is used as hole blocking layer. Alq_3 (10 nm) is used as ETL. Finally, a cathode consisting of 1.2 nm of LiF capped with 100 nm of Al is deposited onto the organic stack. The entire device is fabricated in the same run without breaking the vacuum. In this study, the thicknesses of the different organic layers were kept constant for all the devices. The active area of the devices defined by the overlap of the ITO anode and the metallic cathode was 0.28 cm^2.

The current-voltage-luminance (I-V-L) characteristics of the devices were measured with a regulated power supply (Laboratory Power Supply EA-PS 3032-10B) combined with a multimeter and a 1 cm^2 area silicon calibrated photodiode (Hamamatsu). The spectral emission was recorded with a SpectraScan PR650 spectrophotometer. All the measurements were performed at room temperature and at ambient atmosphere with no further encapsulation of devices.

Synthesis of Compound 2b: To a THF solution (10 mL) of Cp_2ZrCl_2 (286 mg, 1.00 mmol) and 1-(9,9'-dimethylfluoren-2-yl)-8-(5-methyl-2-thienyl)-1,7-octadiyne **1b** (395 mg, 1.00 mmol) was added dropwise (*ca* 1 min), at −78°C, a hexane solution of *n*-BuLi (2.5 M, 0.8 mL, 2.05 mmol). The solution was warmed to room temperature, and stirred overnight. To this solution was added, at −78°C, freshly distilled $PhPBr_2$ (0.22 mL, 1.05 mmol). The solution was allowed to warm to room temperature and stirred for 30 h. The solution was filtered on basic alumina (THF) and the volatile materials were removed under vacuum. The yellow precipitate containing phosphole (^{31}P-{^{1}H} NMR (80 MHz, $CDCl_3$): $\delta = +13.0$) was dissolved in CH_2Cl_2 (20 mL) and elemental sulfur (32 mg, 0.12 mmol) was added to this solution. The solution was stirred for 1 day at room temperature and chromatographed on silica gel (eluent: heptane/ethyl acetate, 95/5, v/v, *Rf* = 0.4). **2b** was obtained as a yellow orange solid (yield = 70 %, 0.7 mmol;, 374 mg). $T_{T\Gamma A10\%}$: 365°C. ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 7.74$ (ddd, ^4J(H,H) = 1.5 Hz, ^3J(H,H) = 6.9 Hz, ^3J(P,H) = 13.8 Hz, 2H, H_{ortho}), 7.58 (m, 1H, $H_{\mathrm{fluorenyl}}$), 7.51 (d, ^3J(H,H) = 7.8 Hz, 1H, $H_{\mathrm{fluorenyl}}$), 7.41–7.31 (m, 4H, 2 H_{meta}, H_{para}, $H_{\mathrm{fluorenyl}}$) 7.28 (s, 1H, $H_{\mathrm{fluorenyl}}$) 7.23–7.20 (m, 2H, $H_{\mathrm{fluorenyl}}$), 7.16 (d, J(H,H) = 7.8 Hz, 1H, $H_{\mathrm{fluorenyl}}$) 7.08 (AB system, ^3J(H,H) = 3.6 Hz, $\Delta\upsilon = 150.1$ Hz, 2H, H_{thienyl}), 2.87 (m, 2H, C = CCH_2), 2.74 (m, 2H, C = CCH_2), 2.38 (s, 3H, $CH_{3\mathrm{thienyl}}$), 1.64 (m, 4H, CH_2), 1.29 (s, 6H, $CH_{3\mathrm{fluorenyl}}$). ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta = 154.3$ (s, $C_{\mathrm{fluorenyl}}$), 153.9 (s, $C_{\mathrm{fluorenyl}}$), 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, $C_{\mathrm{fluorenyl}}$), 139.0 (s, $C_{\mathrm{fluorenyl}}$), 133.4 (d, ^{1}J(P,C) = 82.0 Hz, C_{ipso}), 133.3 (d, ^{2}J(P,C) = 17.1 Hz, $C_{thienyl}$), 132.2 (d, ^{4}J(P,C) = 2.9 Hz, CH_{para}), 131.8 (d, ^{2}J(P,C) = 12.3 Hz, $C_{fluorenyl}$), 130.9 (d, ^{2}J(P,C) = 11.5 Hz, CH_{ortho}), 130.1 (d, ^{1}J(P,C) = 72.0 Hz, C_{α}), 129.1 (d, ^{3}J(P,C) = 12.3 Hz, CH_{meta}), 129.0 (d, ^{1}J(P,C) = 81.7 Hz, C_{α}), 128.6 (d, ^{4}J(P,C) = 5.7 Hz, $CH_{thienyl}$), 128.4 (d, ^{3}J(P,C) = 5.8 Hz, $CH_{fluorenyl}$), 127.8 (s, $CH_{fluorenyl}$), 127.4 (s, $CH_{fluorenyl}$), 126.0 (s, $CH_{thienyl}$), 123.7 (d, ^{3}J(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 = CCH_2), 29.1 (s, C = CCH_2), 27.2 (s, $CH_{3fluorenyl}$), 27.1 (s, $CH_{3fluorenyl}$), 23.2 (s, CH_2), 23.0 (s, CH_2), 15.4 (s, $CH_{3thienyl}$). ^{31}P NMR (121 MHz, CD_2Cl_2): δ = 52.5 (s). HRMS (ESI, *m/z*): $[M + H]^+$ calcd for $C_{34}H_{32}PS_2$, 535.16831; found, 535.1701. Anal. calcd for $C_{34}H_{31}PS_2$: C 76.37 H 5.84 S 11.99; found: C 76.28 H 6.02 S 12.05.

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REFERENCES

1. (a) Skotheims, T. A.; Elsenbaumer, R. L.; Reynolds, J. R. *Handbook of Conducting Polymers, 2nd ed.*; New York: Dekker, **1998**. (b) Müllen, K.; Wegner, G. (eds.) *Electronic Materials: the Oligomer Approach*. Weinheim: Wiley-VCH, **1998**. (c) Müllen, K.; Wegner, G. (eds.) *Electronic Materials: the Oligomer Approach*. Weinheim: Wiley-VCH, **1998**. (d) Cheng, Y.-J.; Yang, S.-H.; Hsu, C.-S. *Chem. Rev.* **2009,** 109, 5868–5923. (e) Usta, H.; Facchetti, A.; Marks, T. J. *Acc. Chem. Res.* **2011,** 44, 501–510.
2. (a) Roncali, J. *Chem. Rev.* **1997,** 97, 173–206. (b) Hissler, M.; Dyer, P.; Réau, R. *Coord. Chem. Rev.* **2003,** 244, 1–44. (c) Mishra, A.; Ma, C.-Q.; Bäuerle, P. *Chem. Rev.* **2009,** 109, 1141–1276.
3. (a) Salzner, U.; Lagowski, J. B. P.; Pickup, G.; Poirier, R. A. *Synth. Met.* **1998,** 96, 177–189. (b) Cyranski, M. K.; Krygowski, T. M.; Katritzky, A. R.; Von Ragué Schleyer, P. *J. Org. Chem.* **2002,** 67, 1333–1338.
4. (a) Schäfer, W.; Schweig, A.; Mathey, F. *J. Am. Chem. Soc.* **1976,** 98, 407–414. (b) Nyulaszi, L. *Chem. Rev.* **2001,** 101, 1229–1246. (c) Mattmann, E.; Mathey, F.; Sevin, A.; Frison, G. *J. Org. Chem.* **2002,** 67, 1208–1213. (d) Mattmann, E.; Mercier, F.; Ricard, L.; Mathey, F. *J. Org. Chem.* **2002,** 67, 5422–5425. (e) Delaere, D.; Nguyen-Nguyen, P.-T.; Nguyen, M. T. *Chem. Phys. Lett.* **2004,** 383, 1–142. (f) Nyulászi, L.; Hollóczki, O.; Lescop, C.; Hissler, M.; Réau, R. *Org. Biomol. Chem.* **2006,** 4, 996–998.
5. (a) Deschamps, E.; Ricard, L.; Mathey. F. *Angew. Chem. Int. Ed. Engl.* **1994,** 11, 1158–1161. (b) Mao, S. S. H.; Tilley, T. D. *Macromolecules* **1997,** 30, 5566–5569. (c) Hay, C.; Hissler, M.; Fischmeister, C.; Rault-Berthelot, J.; Toupet, L.; Nyulaszi, L.; Réau, R. *Chem. Eur. J.* **2001,** 7, 4222–4236. (d) Hay, C.; Fave, C.; Hissler, M.; Rault-Berthelot, J.; Réau. R. *Org. Lett.* **2003,** 19, 3467–3470. (e) Morisaki, Y.; Aiki, Y.; Chujo. Y. *Macromolecules* **2003,** 36, 2594–2597. (f) Fave, C.; Cho, T.-Y.; Hissler, M.; Chen, C.-W.; Luh, T.-Y.; Wu, C.-C.; Réau. R. *J. Am. Chem. Soc.* **2003,** 125, 9254–9255. (g) Baumgartner, T.; Neumann, T.; Wirges. B. *Angew. Chem. Int. Ed.* **2004,** 43, 6197–6201. (h) Baumgartner, T.; Bergmans, W.; Karpati, T.; Neumann, T.; Nieger, M.; Nyulaszi. L. *Chem. Eur. J.* **2005,** 11, 4687–4699. (k) Neumann, T.; Dienes, Y.; Baumgartner, T. *Org. Lett.* **2006,** 8, 495–497. (l) Dienes, Y.; Eggenstein, M.; Neumann, T.; Englert, U.; Baumgartner, T. *Dalton transactions* **2006,** 11, 1424–1433. (m) Sasaki, S.; Mori, T.; Yoshifuji, M. *Heteroatom Chem.* **2006,** 17, 344–349.

6. (a) Bouit, P.-A.; Escande, A.; Szűcs, R.; Szieberth, D.; Lescop, C.; Nyulászi, L.; Hissler, M.; Réau, R. *J. Am. Chem. Soc.* **2012,** 134, 6524–6557. (b) Chen, H.; Delaunay, W.; Yu, L.; Joly, D.; Wang, Z.; Li, J.; Wang, Z.; Lescop, C.; Tondelier, D.; Geffroy, B.; Duan, Z.; Hissler, M.; Mathey, F.; Réau, R. *Angew. Chem. Int. Ed. Engl.* **2012,** 51, 214–217. (c) Joly, D.; Tondelier, D.; Deborde, V.; Delaunay, W.; Thomas, A.; Bhanuprakash, K.; Geffroy, B.; Hissler, M.; Réau, R. *Adv. Funct. Mater.* **2012,** 22, 567–576. (d) Berlinguette, C. P.; Thangadurai, V.; Baumgartner, T. *J. Am. Chem. Soc.* **2011,** 133, 17014–17026. (e) Fadhel, O. ; Szieberth, D. ; Deborde, V. ; Lescop, C. ; Nyulaszi, L. ; Hissler, M. ; Réau, R. *Chem. Eur. J.* **2009,** 15 4914–4924. (f) Fadhel, O.; Benkö, Z. ; Gras, M. ; Deborde, V.; Joly, D. ; Lescop, C.; Nyulászi, L.; Hissler, M. ; Réau, R. *Chem. Eur. J.* **2010,** 16, 11340–11356. (g) Matano, Y.; Nakashima, M.; Imahori, H. *Angew. Chem. Int. Ed.* **2009,** 48, 4002–4005. (h) Su, H.; Fadhel, O.; Yang, C.-J.; Cho, T.-Y.; Fave, C.; Hissler, M.; Wu, C.-C.; Réau, R. *J. Am. Chem. Soc.* **2006,** 128, 983–995. (i) Zhang, L.; Hissler, M.; Bauerle, P.; Lescop, C.; Réau, R. *Organometallics* **2005,** 24, 5369–5376. (j) Fadhel, O.; Gras, M.; Lemaitre, N.; Deborde, V.; Hissler, M; Geffroy, B.; Réau, R. *Adv. Mater.* **2009,** 21, 1261–1265.
7. Geffroy, B.; Lemaitre, N.; Lavigne, J.; Denis, C.; Maisse, P.; Raimond, P. *Nonlinear Opt. Quant. Opt.* **2007,** 37, 9–19.
8. (a) D'Andrade, B. W.; Forrest, S. R. *Adv. Mater.* **2004,** 16, 1585–1595. (b) Kamtekar, K. T.; Monkman, A. P.; Bryce, M. R. *Adv. Mater.* **2010,** 22, 572–582. (c) D'Andrade, B. W. *Nat. Photonics.* **2007,** 1, 33–34. (d) Gather, M. C.; Köhnen, A.; Meerholz, K. *Adv. Mater.* **2011,** 23, 233–248.