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Article

Highly Luminescent 4-Pyridyl-Extended Dithieno[3,2-*b*:2',3'-*d*]phospholes

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ABSTRACT: The unexpectedly challenging synthesis of 4-pyridylextended dithieno[3,2-b:2',3'-d]phospholes via Stille cross-coupling is reported. The optical and electrochemical properties of the phosphorylbridged species were studied experimentally and computationally, and their properties were compared with those of their non-*P*-bridged congeners. The 4-pyridyl-extended dithienophospholes display quantitative luminescence quantum yields in solution and reversible reduction features upon methylation of the pyridine rings. Because of their very high brightness, even in water, 4-pyridyl-extended dithienophospholes are highly promising candidates for new fluorescent probes.



SUPPORTING Information

INTRODUCTION

Over the past decades, there has been a surge in the development of new organic building blocks with useful optoelectronic properties for practical applications in a variety of organic electronics.¹⁻⁵ Some representative molecular platforms include oligothiophenes due to their outstanding charge-transport properties⁶ and viologens for their reversible redox behavior.7 Tuning the properties of these systems via main-group elements is an interesting strategy because it can result in unique changes in terms of the luminescence, supramolecular organization, and electrochemistry.⁸⁻¹⁰ We have been focusing our attention on phosphorus-containing π conjugated species,¹¹ especially the highly luminescent dithieno [3,2-b:2',3'-d] phosphole¹² and the related redoxactive phosphaviologen¹³ scaffolds (Figure 1). In these systems, the addition of phosphorus reduces the energy of the LUMO level via negative hyperconjugation from endocyclic σ^* orbitals with the π^* system.¹¹

Phosphaviologens are strong electron-accepting materials displaying two reversible reduction processes that could successfully be leveraged for photoinduced charge separation¹⁴ and in hybrid batteries.¹⁵ On the contrary, the dithienophosphole oxide scaffold possesses prominent photoluminescence





properties that can be easily tuned by functionalizing the twoand six-positions with aromatic moieties, resulting in an effectively tailorable HOMO–LUMO gap.¹⁶ The resulting compounds display high luminescence quantum yields of up to 80%, and their emissions cover the entire visible spectrum.¹⁷

On the basis of the outstanding properties of these two scaffolds, we were interested to see how the material properties would potentially evolve in a system that combines the favorable electrochemical behavior of phosphaviologens with the exciting photophysical properties of dithienophospholes (Figure 1). It should be mentioned in this context that thienoviologens have been successfully used as electro-fluorochromic materials.^{18–20} Our target species, which can be seen as a hybrid of pyridyl-extended dithienophosphole oxides and phosphorus-bridged thienoviologens, are the subject of this Article, which has also been deposited on ChemRxiv prior to submission.²¹ Their synthesis, optical properties, and electrochemical behavior will be discussed and further evaluated through theoretical calculations.

RESULTS AND DISCUSSION

Synthesis. The first strategy toward pyridyl-functionalized dithienophosphole (PyrDTP, 2) relied on a Suzuki cross-coupling between the commercially available 4-pyridylboronic acid and dibromophosphole 1, synthesized from 2,2'-bithiophene according to literature procedures (Scheme

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Scheme 1. Synthesis of the Targeted Compounds



Figure 2. UV-vis (left) and fluorescence (right) spectra of compounds 2, 4, and 7 (in CH₂Cl₂) and compounds 6 and 8 (in H₂O).

1).^{12,16} Because all Suzuki coupling attempts failed, even under a vast range of conditions (see the Supporting Information), we turned our attention to compound 5, which would be a direct precursor of PyrDTP, as shown for related compounds.²² Pyridyl-substituted bithiophene $(PT)_2$ (4) was synthesized from dibromobithiophene 3 according to Osadnik and Lützen²³ but employing a modified purification procedure. The bromination of 4 was accomplished using N-bromosuccinimide (NBS) in AcOH at 110 °C in 42% yield. Other solvents (CHCl₃, DMF) or bromide sources (Br₂) gave only traces of product. Although the yield of compound 5 is moderate, the bromination of $\tilde{4}$ is selective for the 3,3'-positions, as observed for bithiophenes similar to 4 but possessing alkyl chains at the 5,5'-positions.^{24,25} A definitive proof of the structure of compound 5 was provided by preliminary single-crystal X-ray diffraction. (See the Supporting Information.)

It should be noted that the synthesis of bithiophene **5** was also attempted by means of a Suzuki cross-coupling between 3,3',5,5'-tetrabromo-2,2'-bithiophene or 3,3'-dibromo-5,5'-diiodo-2,2'-bithiophene and 4-pyridylboronic acid, as this route seemed effective for other arylboronic acids, 22,26-28 but no coupling product could be obtained in our case. Unfortunately, a Stille cross-coupling protocol using 4-(trimethylstannyl)pyridine²⁹ did not prove efficient either, nor did the oxidative dehydro C–H coupling of 4-(4-bromothiophen-2-yl)pyridine.³⁰ Moreover, the use of pyridine-*N*-oxides also did not result in any improvements for

either coupling reaction previously mentioned. (See the Supporting Information.)

Unfortunately, the lithiation of compound **5** followed by the reaction with PhPCl₂ toward dithienophosphole oxide **2** according to our established protocols¹² was not effective, possibly due to the very low solubility of bithiophene **5** in the common solvents used for lithiation. (See the Supporting Information.)

With these unforeseen setbacks, we moved back to our initial strategy but using a different type of cross-coupling. To our satisfaction, Stille coupling between 1 and 4-(trimethylstannyl)pyridine using standard conditions (Pd-(PPh₃)₄, refluxing toluene) afforded PyrDTP 2, albeit in low yield (24%). The yield of 2 could be optimized to 37% using tri(2-furyl)phosphine and Pd₂(dba)₃ as a catalytic system (Scheme 1).³¹ PyrDTP was fully characterized by multinuclear NMR spectroscopy and elemental analysis. In particular, its ³¹P NMR spectrum exhibits a single peak at 18.4 ppm characteristic of a π -extended dithieno[3,2-b:2',3'-d]phosphole oxide species.¹⁶

The methylation of the nitrogen centers was accomplished with MeOTf to give $[PyrDTPMe_2]^{2+}[OTf^-]_2$ (6) in 71% yield as its triflate salt. Salient structural features include a singlet at 4.22 ppm for the methyl groups in the ¹H NMR spectrum and a singlet at -79.3 ppm in the ¹⁹F NMR spectrum for the triflate anion. For comparison purposes, **4** was also methylated

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compound	solvent	$\lambda_{\max} \ (nm)^a$	$\varepsilon_{\rm max} \ ({\rm L} \ {\rm mol}^{-1} \ {\rm cm}^{-1})^b$	$\lambda_{\rm em} \ ({\rm nm})^c$	Stokes shift (cm ⁻¹)	$\Phi_{ ext{PL}}{}^{d}$	$B (\mathrm{L} \mathrm{mol}^{-1} \mathrm{cm}^{-1})^{e}$
2	CH_2Cl_2	276, 288 (sh), 327, 415	27 900	507	4400	0.99	27 600
4	CH_2Cl_2	259 (sh), 381	36 300	455	4300	0.22	8000
7	CH_2Cl_2	271, 317, 414	11 300	497	4000	0.81	9200
6	H_2O	289, 305 (sh), 352, 440, 455 (sh)	49 900	504	2900	0.99	49 400
	MeCN	292, 305 (sh), 351, 443, 457 (sh)	50 100	510	2300	0.98	49 100
8	H_2O	256, 284, 431	57 900	501	3200	0.59	34 200
	MeCN	257, 282, 429	58 400	501	3400	0.60	35 000

Table 1. Photophysical Data of the Studied Compounds ($c = 2.5 \times 10^{-5}$ M)

^{*a*}UV/vis absorption peaks; bold values correspond to the $\pi - \pi^*$ transition. ^{*b*}Extinction coefficient associated with the $\pi - \pi^*$ transition. ^{*c*}Emission maxima, excitation at the $\pi - \pi^*$ transition absorption maximum. ^{*d*}Absolute luminescence quantum yield, determined using an integrating sphere. ^{*e*}Brightness, defined as $B = \Phi_{PL} \times \epsilon_{max}$.

under the same conditions to afford $[(PT)_2Me_2]^{2+}[OTf^-]_2~(8)$ in 82% yield.

Compound 2 could also be selectively modified at the phosphorus center by converting it to sulfide PyrDTPsulf (7) using Lawesson's reagent. Compared with 6, compound 7 shows a downfield shift of 8.0 ppm in the ³¹P NMR spectrum, correlating well with related phosphole sulfide species.^{17,32}

Optical Properties. The optical properties of compounds 2, 4, and 6-8 were investigated in different solvents; the results are shown in Figure 2 and are listed in Table 1. All pyridyl-extended phospholes are strongly luminescent in the blue-green to green region of the optical spectrum ($\lambda_{\rm em} = 497$ to 510 nm) and show a significant red shift compared with phosphole 1, as previously observed for phospholes with extended π -conjugation.¹⁶ The maximum emission of 2 (λ_{em} = 507 nm) is very similar to the emission of a related 2-picolylextended dithienophosphole ($\lambda_{em} = 511 \text{ nm}$).¹⁶ Compound 4 and its viologen congener 8 are also luminescent, as previously reported.^{18,19,33,34} The tethering of the thiophene rings with an oxyphosphoryl moiety has a strong influence on the optical properties: A red shift of $\Delta \lambda = 34$ nm (absorption) and $\Delta \lambda =$ 52 nm (emission) is observed between 4 and 2. This effect is much less pronounced for the methylviologen analogs 6 and 8 $(\Delta \lambda = 9 \text{ to } 14 \text{ nm in absorption and } 3 \text{ to } 9 \text{ nm in emission,}$ depending on the solvent). The absorption coefficients for the phospholes are in the typical range of 11 000-50 000 L·mol⁻¹. cm⁻¹, which is slightly lower compared with the nonphosphole analogs 4 and 8. Stokes shifts vary from 2200 to 4400 cm^{-1} , similar to previously reported dithienophospholes,¹⁶ and a lowering of $1000-1400 \text{ cm}^{-1}$ is observed upon methylation.

The most striking features of pyridyl-extended phosphole oxides, N-quaternized or not, are their very pronounced emission properties. Compound 2 displays a quantitative luminescence quantum yield in CH2Cl2. Upon N-methylation of the pyridine rings, the quantum yield remains quantitative in MeCN and even in water, in sharp contrast with the quantum yields of 4 ($\Phi_{PL} = 0.22$ in CH₂Cl₂, 0.10 in 40% aq MeOH,³³ and 0.11 in DMF³⁴) and thienoviologen 8 ($\Phi_{PI} = 0.60$ in H₂O compared with 0.52 for diprotonated 4 in 40% aq MeOH 33). Compared with P-oxide 2, the quantum yield of sulfide analogue 7 is lower (Φ_{PL} = 0.81 in CH₂Cl₂) but is still quite high. As a result, the pyridyl-extended dithienophospholes display very high brightness values (up to 50 000 L·mol⁻¹· cm^{-1}), with the viologen species 6 having the highest observed value in this series. Given that both phosphole-oxide-based compounds 2 and 6 have quantum yields near unity, the doubling of the brightness from 2 to 6 can only be attributed to the significantly larger extinction coefficient for the latter that is also supported by time-dependent density functional theory (TD-DFT) calculations via increased oscillator strengths for the respective transitions (vide infra). These values are considerably superior to commonly used fluorophores (including most coumarins, naphthalimides, cyanines, and BODIPY-based dyes) and are comparable to xanthene-based fluorophores (rhodamine and fluorescein derivatives, *B* usually in the 20 000–90 000 range).^{35,36}

Electrochemical Properties. The redox properties of pyridyl-functionalized dithienophospholes were assessed using cyclic voltammetry (Figure 3).



Figure 3. Cyclic voltammograms (referenced vs Ag/AgCl) of compounds **2**, **4**, and **6–8** in DMF containing 0.1 M $[NBu_4][PF_6]$ as the supporting electrolyte (c = 1 to 2 mg·mL⁻¹, scan rate: 100 mV·s⁻¹). For cyclic voltammograms at different scan rates, see the Supporting Information.

Compound 4 shows two successive quasi-reversible reduction events in DMF ($E_{\text{red},1} = -1.58$ V and $E_{\text{red},2} =$ -1.80 V). The same behavior is observed for *P*-oxide 2 and its sulfide congener 7 ($E_{\text{red},1} = -1.22$ and -1.21 V and $E_{\text{red},2} =$ -1.53 and -1.52 V, respectively). The shift toward lower potentials for compounds 2 and 7 compared with compound 4 was also observed for phosphaviologens compared with viologens and can be attributed to the $\sigma^* - \pi^*$ interaction in the phosphoryl-bridged species.¹³ Notably, the reversibility was found to depend strongly on the solvent: In CH₂Cl₂, only irreversible reductions were found for compound 4, whereas for phospholes 2 and 7, the second reduction peak became irreversible. (See the Supporting Information.) This points toward solubility issues and deposition on the electrode in this solvent. When the nitrogen atoms are methylated, only one reduction event is detected ($E_{\rm red} = -0.75$ V for 8 and -0.59 V for 6) in addition to a considerable shift toward lower potentials. Whereas most viologen derivatives exhibit two distinct reduction peaks, such behavior was already observed for closely related derivatives of compound 8.37 This single-

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Figure 4. Calculated HOMO and LUMO energy levels (B3LYP/6-31G(d) level of theory)³⁵ of dithienophospholes, thienoviologens, and phosphaviologens. Calculations were performed in a vacuum for neutral species and in H₂O for cationic species.



Figure 5. Frontier orbitals of 2, 4, 7 (PCM in CH_2Cl_2), 6, and 8 (cations only; PCM in MeCN). Isovalue is 0.02. The TD-DFT-derived contribution of the HOMO-LUMO transition to the lowest excited state is indicated beside the arrows.

step two-electron reduction event may also consist of two very close one-electron reduction peaks. Viologen **8** displays a quasi-reversible behavior, whereas phosphole **6** exhibits complete electrochemical reversibility for scan rates between 10 and 200 mV·s⁻¹, as shown by the constant peak potential within this range, making it a promising species for battery applications.¹⁵

Density Functional Theory Calculations. The electronic properties of pyridyl-extended dithienophospholes were investigated by DFT calculations (B3LYP/6-31G(d) level of theory)³⁸ and were compared with related dithienophosphole oxides, phosphaviologens, and thienoviologens. Calculations were performed in a vacuum and DMF and in a CH_2Cl_2

environment for neutral species as well as in H_2O and MeCN for cationic species. The polarization continuum model (PCM) was employed to simulate solvation effects. Compared with the 2,6-diphenyl-substituted dithienophosphole 9,¹⁶ the replacement with a 4-pyridyl moiety results in a lowering of both HOMO and LUMO levels by the same extent, resulting in a similar energy gap but a stabilized LUMO level (Figure 4). A smaller stabilization of the LUMO level of 2 compared with that of 4 is observed, along with a small reduction of the energy gap. This can be explained by the additional rigidification of the scaffold provided by the bridging phosphorus. No significant difference in terms of the energy levels was seen between *P*-oxide 2 and *P*-sulfide 7. On the contrary, *N*-

compound	solvent	$\lambda_{\max,\exp} (\mathrm{nm})^a$	$\lambda_{\rm max,DFT} \ ({\rm nm})^b$	f^{c}	$E_{\rm LUMO,exp} ~({\rm eV})^d$	$E_{\rm LUMO,DFT} ~({\rm eV})^e$
2	CH_2Cl_2	415	442	0.889	-2.80	-2.53
4	CH_2Cl_2	381	409	1.319	-2.44	-2.26
7	CH_2Cl_2	414	442	0.783	-2.81	-2.55
6	H ₂ O	440	497	1.371		
	MeCN	443	498	1.374	-3.40	-3.57
8	H ₂ O	431	481	1.645		
	MeCN	429	482	1.649	-3.22	-3.43

^{*a*}Absorption maximum from UV/vis spectroscopy. (See Table 1.) ^{*b*}Absorption maximum from TD-DFT calculations. ^{*c*}Oscillator strength. ^{*d*}Energy of the LUMO level found from the onset of the first reduction potential in cyclic voltammetry (in DMF) and calculated by referencing it to the energy level of Ag (-3.91 eV). ^{*e*}Energy of the LUMO level found through DFT calculations (PCM in DMF).

methylation led to a further stabilization of the HOMO and LUMO levels as well as to an important reduction of the energy gap, showcasing the strong electron-accepting character of viologens 6 and 8. Finally, compared with the phosphaviologen series (10 and 11), the LUMO level is less stabilized, but the energy gap is smaller (Figure 4).

Time-dependent density functional theory (TD-DFT) calculations were also performed at the B3LYP/6-31G(d) level of theory;³⁸ solvent effects were taken into account using the PCM solvation model, and the results are shown in Figure 5 and Table 2. For all compounds, the main absorption band, which corresponds to the $\pi - \pi^*$ transition (see the Supporting Information), nearly exclusively stems from HOMO to LUMO transitions, as observed for other fluorophores including alizarin³⁹ and coumarin derivatives.⁴⁰ The trend in extinction coefficients is quite well reflected by the corresponding oscillator strength values. The >50% larger value for the viologen species 6 (compared with that of 2) can be correlated with the increased polarity of its scaffold that leads to a more pronounced change in dipole moment between the ground and excited states. The calculated absorption maxima are systematically overestimated by 27 to 28 nm for the neutral species and 50-57 nm for the cationic species, but such discrepancies are not uncommon for TD-DFT calculations involving dyes.^{41,42} Finally, for all compounds, a good correlation is observed between the LUMO levels obtained from cyclic voltammetry and those obtained through DFT calculations, with a systematic slight difference of ~ 0.2 eV (Table 2).

CONCLUSIONS

In conclusion, we have established a synthetic protocol toward pyridyl-extended dithienophospholes in the hope of obtaining a compound combining the electrochemical properties of phosphaviologens with the optical properties of dithieno 3,2b:2',3'-d phospholes. Both properties are indeed combined in this new scaffold, which displays electrochemically reversible features upon methylation of the pyridine rings as well as prominent optical properties including quantitative quantum yields in organic and aqueous solvents in conjunction with reasonably large Stokes shifts. This evolves the previously established features of π -extended dithienophospholes and makes pyridyl-extended dithienophospholes attractive candidates for potential fluorescent (bio)probes, next to organic batteries. In particular, modifications at the nitrogen center do not seem to affect quantum yields, thus providing a convenient grafting point for fluorescence labeling. Further developments may reveal the potential of pyridine-extended dithienophospholes in materials science and for imaging purposes. These studies are ongoing in our laboratory.

EXPERIMENTAL SECTION

General Materials, Instruments, and Methods. All manipulations were performed under an argon atmosphere using standard Schlenk techniques. Solvents were dried with an MBraun Solvent Purification System. An oil bath was used for reactions requiring heating. Starting materials and reagents were purchased from Sigma-Aldrich, Oakwood Chemical, or Strem Chemicals and used without further purification. Compounds 1,^{12,16} 3,⁴³ and 4-(trimethylstannyl)pyridine²⁹ were synthesized according to literature procedures. Flash column chromatography was performed using a SiliaFlash M60 silica gel (60–120 μ m). Thin-layer chromatography was performed on silica gel 60 F_{254} precoated plates. ¹H, ¹³C{¹H}, ³¹P{¹H}, and ¹⁹F{¹H} NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. Chemical shifts were referenced to residual nondeuterated solvent peaks (CDCl₃: 7.26 ppm for ¹H and 77.16 ppm for ¹³C, CD₃CN: 1.94 ppm for ¹H and 1.32 ppm for ¹³C). Elemental analysis was performed using an Elementar vario EL cube. Electrospray ionization (ESI) high-resolution mass spectrometry (HRMS) was performed on a ThermoFisher Orbitrap Elite spectrometer. Optical spectroscopy was performed on an Agilent Cary 5000 UV-vis spectrophotometer. Fluorescence spectroscopy was performed on an Edinburgh Instruments FS5 spectrofluorometer. Cyclic voltammetry was performed on a Metrohm Autolab PGSTAT204 potentiostat connected to a three-electrode cell with glassy carbon as a working electrode, Pt wire as a counter electrode, and Ag/AgCl as a reference electrode. Solvents were degassed with argon, and the working electrode was polished with alumina before each experiment. DFT calculations were performed with Gaussian 09.38 Vibrational harmonic frequency analysis was performed to ensure that there were no imaginary frequencies.

Synthetic Procedure for $(PT)_2$ (4). A mixture of 5,5'-dibromo-2,2'-bithiophene (10.0 g, 30.9 mmol, 1.0 equiv), 4-pyridylboronic acid (8.0 g, 64.9 mmol, 2.1 equiv), Pd(PPh₃)₄ (1.79 g, 1.55 mmol, 0.05 equiv), and K₂CO₃ (25.6 g, 185 mmol, 6.0 equiv) was stirred in toluene/MeOH/H₂O (500/250/80 mL) at 85 °C for 48 h. The solvent was removed in vacuo, and the resulting solid was washed with H₂O and dried. Column chromatography (1:1 CH₂Cl₂/EtOAc, then 4:1 CH₂Cl₂/MeOH) followed by washing with toluene (50 mL), then acetone (50 mL) afforded 4 as a yellow solid (6.56 g, 20.5 mmol, 66%). R_f 0.66 (9:1 CH₂Cl₂/MeOH). ¹H NMR (400 MHz, CDCl₃) δ 8.62 (dd, J = 4.5, 1.7 Hz, 4H), 7.48–7.44 (m, 6H), 7.25 (s, 2H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 150.7, 140.9, 140.6, 138.5, 126.4, 125.6, 119.7. Characterization is in accordance with the literature. ^{23,33,34,44,45}

Synthetic Procedure for Compound 5. Compound 4 (3.0 g, 9.36 mmol, 1.0 equiv) was dissolved in AcOH (150 mL). NBS (5.0 g, 28.1 mmol, 3.0 equiv) was added. The resulting mixture was stirred at 110 °C for 48 h. The solvent was removed in vacuo, and the resulting solid was washed with H₂O and dried. Column chromatography (100:0 to 95:5 CH₂Cl₂/MeOH) afforded 5 as an orange solid (1.86 g, 3.89 mmol, 42%). R_f 0.70 (9:1 CH₂Cl₂/MeOH). ¹H NMR (400 MHz, CDCl₃) δ 8.61 (dd, J = 4.5, 1.7 Hz, 4H), 7.47–7.44 (m, 6H), 7.47 (dd, J = 4.5, 1.7 Hz, 4H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ

Synthetic Procedure for PyrDTP (2). A mixture of phosphole 1 (242 mg, 0.54 mmol, 1.0 equiv), 4-(trimethylstannyl)pyridine (392 mg, 1.62 mmol, 3.0 equiv), tri(2-furyl)phosphine (23 mg, 0.10 mmol, 0.18 equiv), and Pd₂(dba)₃ (30 mg, 0.03 mmol, 0.06 equiv) was refluxed in toluene (10 mL) for 15 h. The solvent was removed in vacuo. Column chromatography (95:5 to 88:12 EtOAc/MeOH) afforded 2 as an orange solid (89 mg, 0.20 mmol, 37%). Rf 0.34 (4:1 EtOAc/MeOH). ¹H NMR (400 MHz, CDCl₃) δ 8.64 (dd, J = 4.6, 1.6 Hz, 4H), 7.80 (ddd, J = 13.6, 8.2, 1.2 Hz, 2H), 7.59 (td, J = 7.5, 1.7 Hz, 1H), 7.57 (d, J = 2.8 Hz, 2H) 7.48 (td, J = 7.6, 3.4 Hz, 2H), 7.42 (dd, J = 4.6, 1.6 Hz, 4H). ³¹P{¹H} NMR (162 MHz, CDCl₃) δ 18.4. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 150.9, 146.0 (d, J = 14.1 Hz), 145.9 (d, J = 22.9 Hz), 140.7 (d, J = 110.8 Hz), 140.3, 133.2 (d, J = 3.0 Hz), 131.0 (d, J = 11.6 Hz), 129.4 (d, J = 13.2 Hz), 128.8 (d, J = 109.1 Hz), 124.1 (d, J = 14.3 Hz), 119.7. Anal. Calcd for C₂₄H₁₅N₂OPS₂: C, 65.14; H, 3.42; N, 6.33; S, 14.49. Found: C, 65.39; H, 3.05; N, 6.71; S, 14.53. HRMS (ESI) m/z: [M + H]⁺ calcd for C₂₄H₁₆N₂OPS₂ 443.0442; found 443.0442.

Synthetic Procedure for [PyrDTPMe2]²⁺[2OTf⁻]2 (6). A solution of 2 (80 mg, 0.18 mmol, 1.0 equiv) in DCM (15 mL) was cooled to 0 °C. MeOTf (50 µL, 0.45 mmol, 2.5 equiv) was added. The resulting mixture was allowed to warm to rt for 15 h. The precipitate was filtered, washed with a small amount of cold MeCN, and dried to afford 6 (99 mg, 0.13 mmol, 72%) as an orange solid. ¹H NMR (400 MHz, CD₃CN) δ 8.53 (d, J = 6.6 Hz, 4H), 8.17 (d, J = 2.9 Hz, 2H), 8.10 (d, J = 6.6 Hz, 4H), 7.82 (dd, J = 13.9, 7.6 Hz, 2H), 7.67 (t, J = 7.2 Hz, 1H), 7.54 (td, J = 7.4, 2.9 Hz, 2H), 4.22 (s, 6H). ${}^{31}P{}^{1}H$ NMR (162 MHz, CD₃CN) δ 15.7. ${}^{13}C{}^{1}H$ NMR (101 MHz, CD₃CN) δ 150.1 (d, J = 21.8 Hz), 148.8, 146.4, 144.2 (d, J = 43.6 Hz), 143.6 (d, J = 50.8 Hz), 134.5 (d, J = 3.0 Hz), 131.9 (d, J = 11.7 Hz), 130.8 (d, J = 14.0 Hz), 130.4 (d, J = 13.6 Hz), 129.3 (d, J = 110.9 Hz), 123.7, 122.2 (q, J = 321.1 Hz, appears as a doublet due to the low intensity), 48.5. ${}^{19}F{}^{1}H{}$ NMR (377 MHz, CD₂CN) δ -79.3. Anal. Calcd for C28H21F6N2O7PS4: C, 43.64; H, 2.75; N, 3.63; S, 16.64. Found: C, 43.48; H, 2.38; N, 3.75; S, 16.45. HRMS (ESI) m/z: $[M]^{2+}$ calcd for C₂₆H₂₁N₂OPS₂/2 236.0417; found 236.0412.

Synthetic Procedure for PyrDTPsulf (7). Compound 2 (56 mg, 0.13 mmol, 1.0 equiv) was partially dissolved in toluene (15 mL). Lawesson's reagent (26 mg, 0.06 mmol, 0.5 equiv) was added. The resulting mixture was refluxed for 18 h. The solvent was removed in vacuo. Column chromatography (100:0 to 85:15 EtOAc/MeOH) afforded 7 as an orange solid (35 mg, 0.08 mmol, 62%). R_f 0.63 (4:1 EtOAc/MeOH). ¹H NMR (400 MHz, CDCl₃) δ 8.63 (dd, J = 4.6, 1.6 Hz, 4H), 7.86 (ddd, J = 15.4, 8.3, 1.1 Hz, 2H), 7.58 (d, J = 2.9 Hz, 2H), 7.55 (td, J = 7.6, 2.1 Hz, 1H), 7.47 (td, J = 7.8, 3.3 Hz, 2H), 7.44 (dd, J = 4.6, 1.6 Hz, 4H). ³¹P{¹H} NMR (162 MHz, CDCl₃) δ 26.7. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 150.7, 146.0 (d, J = 14.7 Hz), 144.3 (d, J = 19.0 Hz), 143.6 (d, J = 93.2 Hz), 140.4, 132.8 (d, J = 3.0 Hz), 130.9 (d, J = 15.4 Hz), 119.6 HRMS (ESI) m/z: [M + H]⁺ calcd for C₂₄H₁₆N₂PS₃ 459.0213; found 459.0217.

Synthetic Procedure for $[(PT)_2Me_2]^{2+}[OTf^-]_2$ (8). A solution of 4 (200 mg, 0.62 mmol, 1.0 equiv) in DCM (100 mL) was cooled to 0 °C. MeOTf (171 μL, 1.56 mmol, 2.5 equiv) was added. The resulting mixture was allowed to warm to rt for 15 h. The precipitate was filtered, washed with a small amount of cold MeCN, and dried to afford 8 as an orange solid (332 mg, 0.51 mmol, 82%). ¹H NMR (400 MHz, CD₃CN) δ 8.50 (d, *J* = 6.9 Hz, 4H), 8.10 (d, *J* = 6.9 Hz, 4H), 8.00 (d, *J* = 4.1 Hz, 2H), 7.64 (d, *J* = 4.1 Hz, 2H), 4.22 (s, 6H). ¹³C{¹H} NMR (101 MHz, CD₃CN) δ 149.0, 146.2, 143.5, 138.3, 134.1, 129.4, 123.4, 122.3 (q, *J* = 320.9 Hz, appears as a doublet due to the low intensity), 48.4. ¹⁹F{¹H} NMR (377 MHz, CD₃CN) δ -79.3. HRMS (ESI) *m*/*z*: [M]²⁺ calcd for C₂₀H₁₈N₂S₂/2 175.0456; found 175.0451.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c01369.

Details of attempted (unsuccessful) reactions toward pyridyl-extended dithienophospholes, X-ray crystallographic data for **5**, additional cyclic voltammetry data, DFT computational data, and copies of NMR spectra of all new compounds (PDF)

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Notes

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