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Bis(azidophenyl)phosphole Building Block for Extended π -Conjugated Systems

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Novel bis(azidophenyl)phosphole sulfide building block **8** has been developed to give access to a plethora of phosphole-containing π -conjugated systems in a simple synthetic step. This was explored for the reaction of the two azido moieties with phenyl-, pyridyl- and thienylacetylenes, to give bis(aryltriazolyl)-extended π -systems, having either the phosphole sulfide (**9**) or the phosphole (**10**) group as central ring. These conjugated frameworks exhibit intriguing photophysical and electrochemical properties that vary with the nature of the aromatic end-group. The λ^3 -phospholes **10** display blue fluorescence ($\lambda_{em} = 460-469$ nm) with high quan-

Introduction

Neglected for decades, phosphorus is now recognized as a valuable component in π -conjugated molecular frameworks.^[1] The phosphole ring, in particular, has potential as a building block in organic materials,^[2] as exemplified by the organic light-emitting devices (OLEDs) based on chlorido(dithienylphosphole)gold(I) complex 1 (Figure 1).^[3] The electronic structure^[4] of the phosphole ring combines a low but not negligible degree of aromaticity, originating from hyperconjugation between the carbon-based π -system and the exocyclic $\sigma(P-R)$ orbital,^[5] with a tunable $\lambda^3 \sigma^3$ -phosphorus center.^[3b] This combination provides a handle to fine-tune the photophysical properties of phosphole-containing π -systems by influencing the extent of conjugation over the diene moiety.^[6] There are limitations to this modification, as 2,5-bis(aryl)phospholes having a $\lambda^5 \sigma^4$ -phosphorus center generally suffer from severely reduced luminescence quantum yields,^[2,3b] making them unsuitable for electronic devices. However, a viable option is to modify the

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tum yield ($\Phi_{\rm F} = 0.134$ –0.309). The radical anion of pyridylsubstituted phosphole sulfide **9b** was observed with UV/Vis spectroscopy. TDDFT calculations on the extended π -systems showed some variation in the shape of the HOMOs, which was found to have an effect on the extent of charge transfer, depending on the aromatic end-group. Some fine-tuning of the emission maxima was observed, albeit subtle, showing a decrease in conjugation in the order thienyl < phenyl < pyridyl. These results show that variations in the distal ends of such π -systems have a subtle but significant effect on photophysical properties.

phosphole lone-pair participation in the π -system by increasing the steric bulk around the phosphorus centre.^[7] Such attempts to generate fused phosphole-thiophene building block 2 did result in varying HOMO-LUMO gaps, but not in the desired fine-tuning of photophysical properties.^[8] The π -conjugated backbone itself can also be modified, which is a commonly applied strategy for carbonbased π -systems.^[9] This approach has been explored for the thiophene-substituted phosphole 1^[2] and the thiophenephosphole-thiophene-fused π -systems $3^{[10]}$ by functionalization of the thiophene ring. Also noteworth is the π -system extension of 2,5-diethynylphosphole with phenyltriazolyl moieties through application of the copper-catalyzed 1,3-dipolar Huisgen reaction with phenyl azide.^[11] This approach enabled further fine-tuning of the photophysical properties by introducing various substituents at the para position of the distal phenyl groups. Here, we examine how far-reaching the electronic effect may be with subtle changes in the backbone.



Figure 1. Examples of phosphole-containing π -conjugated molecular frameworks.

As a novel phosphole-containing building block we chose 2,5-diarylphosphole **8**, the first phosphole-containing compound bearing azido moieties. These moieties enable

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access to diverse derivatives by application of copper-catalyzed 1,3-dipolar Huisgen addition^[12] between the azido groups and various aromatic acetylenes. The present study reports the synthesis and photophysical properties of a select number of such derivatives.

Results and Discussion

Synthesis of Bis(azidophenyl)phosphole Building Block 8

Targeted building block **8** was synthesized by the multistep procedure depicted in Scheme 1. The phosphole moiety was introduced in the third step using a Fagan–Nugent reaction,^[13] an efficient and elegant method for heterocycle synthesis, particularly phospholes.^[1,14] Bis(imine) **5** was used as the reactant, since the Fagan–Nugent reaction had proven incompatible with primary amine and azide functionalities.



Scheme 1. Synthesis of bis(azidophenyl)phosphole sulfide **8**. (a) Pd(OAc)₂, PPh₃, THF, TEA, r.t., 16 h; (b) benzophenone imine, NaOtBu, Pd₂dba₃, BINAP, toluene, 80 °C, 48 h; (c) ZrCp₂, THF, -78 °C (1 h) \rightarrow r.t. (3 h); (d) CuCl, THF, 0 °C, 0.5 h; (e) PhPCl₂, THF, 0 °C \rightarrow r.t., 18 h; (f) S₈, THF, r.t., 5 h; (g) HCl, H₂O, THF, 66 °C, 2 h; (h) NaNO₂, HCl, H₂O, THF, -5 °C, 10 min; (i) NaN₃, NaOAc, H₂O, THF, -5 °C, 2 h.

Bis(imine) **5** was efficiently prepared by Sonogashira coupling of octa-1,7-diyne with 2 equiv. of 1-bromo-3-iodobenzene, followed by a Buchwald–Hartwig coupling with benzophenone imine in 98% yield. Treatment of **5** with ZrCp₂ resulted in the formation of a distinctly red transient zirconocyclopentadiene species that gave, after transmetallation with CuCl and addition of PhPCl₂, the desired bis-(imino)phosphole. Oxidation of this species with elemental

sulfur afforded corresponding phosphole sulfide 6; this step proved to be necessary to prevent oxidation during the subsequent two steps that employ aqueous media. Acidic hydrolysis of 6 afforded primary bis(amine) 7, which was transformed into the corresponding bis(diazonium) salt and reacted with sodium azide to give target bis(azidophenyl)phosphole sulfide 8 in 31% isolated yield. The structure of 8 was unequivocally established by X-ray crystal structure determination (Figure 2). Characteristic bond lengths, angles and torsion angles of 8 are given in Table 1. The most intriguing characteristic of the crystal structure is the fact that both azido moieties are pointing in more or less the same direction. As will be discussed later, this "downward" (or syn) orientation of the two aromatic substituents at these positions is the most stable possibility for the extended π -systems. The interplanar angles between the phenyl rings and the central phosphole are 51.48(10)° and 22.02(9)°, respectively, which restricts efficient inter-ring π orbital overlap. As a consequence, the C–C bonds of the π conjugated path are only slightly smaller than regular single bonds, and the corresponding C=C bonds are only slightly longer than unconjugated double bonds (see Table 1).



Figure 2. Crystal structure of bis(azidophenyl)phosphole sulfide 8 with numbering of the atoms. Hydrogen atoms are omitted for clarity, and ellipsoids are at 50% probability.

Table 1. S	Selected	bond	lengths	[Å],	angles,	and	torsion	angles	[°] (of
bis(azido	phenyl)	ohospł	nole sulf	fide	8 in the	e crys	stal. ^[a]			

C8–C7	1.353(2)	C7–C2	1.498(2)
C2C1	1.363(2)	C1C15	1.473(2)
C8–C9	1.479(2)	P1-C1	1.8225(17)
P1-C8	1.8038(18)	P1-C21	1.8309(18)
C1-P1-C8	93.44(8)	C8-P1-C21	103.54(8)
C1-P1-C21	106.08(8)		
P1-C1-C15-C16	20.3(2)	C2C1P1C8	-5.25(13)
P1-C8-C9-C10	53.8(2)	P1C1C2C7	2.93(18)
C1-C2-C7-C8	2.0(2)		

[a] Atom numbering in accordance with Figure 2.

"Click" Chemistry

Extension of the π -system of 8 was accomplished using copper-catalyzed 1,3-dipolar Huisgen addition, coined click chemistry,^[12] by a reaction with phenyl-, 2-pyridyl- and 2thienyl-substituted acetylenes using [Cu(NCMe)₄][PF₆] as the catalyst and 2,6-lutidine as the ligand (Scheme 2).^[12b] The resulting products, obtained in 82–99% yield, are representative examples with the phenyl (9a), electron-rich pyridine (9b), and thiophene (9c) rings introduced at the distal ends of the extended π -system. The sulfur atoms were effectively removed from the phosphorus center in 71-100%yield, using P(NMe₂)₃, to obtain the corresponding $\lambda^3 \sigma^3$ phospholes 10a-c, which are expected to exhibit higher quantum yields than sulfur-protected analogues 9. Both the phosphole and phosphole sulfide based extended π -systems exhibit distinctive ³¹P NMR chemical shifts, which are not influenced by the aromatic end-groups [$\delta^{31}P = 54.4$ (9a),



Scheme 2. Extension of the π -system by application of click chemistry. (a) phenyl-, 2-pyridyl- or 2-thienylacetylene, [Cu(NCMe)₄] [PF₆], 2,6-lutidine, CH₂Cl₂, r.t., 48 h; (b) P(NMe₂)₃, toluene, reflux, 25 h. lp = lone pair.

Table 2. Photophysical data for phosphole sulfides **9a-c** and phospholes **10a-c**.

	$\lambda_{abs} [nm]^{[a]}$	$\varepsilon [\mathrm{M}^{-1} \mathrm{cm}^{-1}]^{[a]}$	$\lambda_{em} \ [nm]^{[b]}$	Φ _F r.t. ^[b] or 4 K ^[c]	τ [ns] r.t. ^[d] or 4 K ^[e]
9a	248	6.08×10^{4}	303	0.0019 ^[b]	n.d. ^[g]
	326 (sh)	8.23×10^{3}	416 ^[f]		
	385 (sh)	4.46×10^{3}			
9b	286	4.66×10^{4}	302	0.0036 ^[b]	4.6 ^[d]
	324 (sh)	3.06×10^{4}	414 ^[f]	0.0055 ^[c]	7.8 ^[e]
	382 (sh)	1.66×10^{4}			
9c	275	1.96×10^{4}	302	0.00071 ^[b]	n.d. ^[g]
	339 (sh)	3.58×10^{3}	416 ^[f]		
	382 (sh)	2.12×10^{3}			
10a	290 (sh)	2.63×10^{4}	463	0.273 ^[b]	3.8 ^[d]
	355	1.62×10^{4}		0.484 ^[c]	6.8 ^[e]
10b	286	2.81×10^{4}	469	0.134 ^[b]	3.7 ^[d]
	355	1.13×10^{4}		0.209 ^[c]	5.7 ^[e]
10c	276	3.23×10^{4}	460	0.309 ^[b]	2.7 ^[d]
	356	1.02×10^4		0.731 ^[c]	6.3 ^[e]

[a] Measured in CH₂Cl₂ as 10^{-6} M solutions. [b] At r.t., determined for 10^{-5} M phosphole sulfides **9a–c** and 10^{-7} M phospholes **10a–c** in cyclohexane, using perylene ($\Phi_{\rm F} = 94\%$) as the reference. [c] At 4 K, computed according to Equation (1). [d] At r.t., determined for 10^{-4} M phosphole sulfides **9a–c** and 10^{-6} M phospholes **10a–c** in cyclohexane. [e] At 4 K, determined for 10^{-4} M phosphole sulfides **9a–c** and 10^{-6} M phospholes **10a–c** in cyclohexane. [f] Recorded as a 10^{-4} M solution. [g] Not determined.

54.4 (9b), 54.4 (9c), 13.6 (10a), 13.5 (10b), 13.8 (10c) ppm].

Next, we set out to analyze the electronic structure and photophysical properties of the extended π -systems **9a–c** and **10a–c** by UV/Vis absorption and fluorescence spectroscopy, cyclic voltammetry, spectroelectrochemistry, and DFT calculations in order to investigate the influence of the aromatic end-groups on the core. All spectroscopic data are summarized in Table 2.

UV/Vis Absorption and Fluorescence Spectroscopy

The electronic absorption spectra of phosphole sulfides 9a-c show broad unresolved low-energy transitions in the range $\lambda_{abs} = 300-420$ nm, wherein two shoulders could be identified (see Figure 3a). Their fluorescence spectra show emission from two distinct species. The broad emission band around $\lambda_{em} = 415$ nm is dominant at higher concentrations (10⁻⁴ m; Figure 4a), whereas the one at λ_{em} = 302 nm becomes dominant at lower concentrations (10^{-5} M ; Figure 4b). At higher concentration, two excitation bands are observed; one at $\lambda_{\text{exc}} = 261-266$ nm and a broad band around $\lambda_{\text{exc}} = 340$ nm, whereas two higher-energy bands are present at $\lambda_{exc} = 229-230$ nm and $\lambda_{exc} = 279-281$ nm at lower concentration. Quantum yields are very low for the phosphole sulfides and could be determined only at 10^{-4} M $[\Phi_{\rm F} = 0.0019 \ (9a), \ 0.0036 \ (9b), \ 0.00071 \ (9c); \ Table 2], \ since$ the fluorescence intensity at lower concentrations was too low for accurate quantum yield determination.



Figure 3. Normalized UV/Vis absorption spectra for (a) phosphole sulfides **9a** (blue), **9b** (green) and **9c** (red) and (b) phospholes **10a** (blue), **10b** (green) and **10c** (red). Recorded as 10^{-5} M solutions in CH₂Cl₂.

The lowest-energy absorption maxima of the desulfurized phospholes **10a–c** (Figure 3b) exhibit a lowest-energy emission, which is more resolved when compared to their sulfur-protected analogues. These lowest-energy maxima are located approximately halfway between the two shoulders observed for the corresponding sulfur-protected analogue. A pronounced bathochromic shift is observed in the fluorescence maxima (Figure 5), which shows a 160–167 nm shift to longer wavelengths relative to the emission maxima of monomeric **9a–c** (Figure 4b). Interestingly, the phosphole sulfide based π -systems **9a–c** exhibit both absorption and emission maxima of much higher energy than the related 2,5-diarylphosphole sulfides,^[6] suggesting that the



Figure 4. Normalized emission (solid) and excitation (dotted) spectra for phosphole sulfides **9a** (blue), **9b** (green) and **9c** (red); (a) recorded as 10^{-4} M solutions in THF ($\lambda_{exc} = 260-266$ nm; $\lambda_{em} = 405-410$ nm); (b) recorded as 10^{-5} M solutions in THF ($\lambda_{exc} = 230$ nm; $\lambda_{em} = 302$ nm).

conjugation in these systems is somehow disrupted. In contrast, phospholes **10a–c** behave similarly to related diarylphosphole π -systems (λ^3 analogues of **1**).^[6] These phospholes emit blue-green light and exhibit sizeable Stokes shifts of 104–109 nm.



Figure 5. Normalized emission spectra of phospholes **10a** (blue), **10b** (green) and **10c** (red). Recorded as 10^{-7} M solutions in cyclohexane ($\lambda_{exc} = 350-356$ nm).

As expected, fluorescence quantum yields are dramatically enhanced for the σ^3 -phospholes **10a–c** [$\Phi_F = 0.273$ (**10a**), 0.134 (**10b**), 0.309 (**10c**); Table 2]. Notably, these quantum yields are among the highest reported thus far for 2,5-diarylphosphole-based π -systems.^[6]

Excited-state lifetimes (τ) for the emission from phospholes **10a**-**c** were determined from single exponential fits for the emission decay curves recorded between 4 K and room temperature (Figure 6). These lifetimes are all around 6 ns up to approximately 120 K, above which they gradually become shorter. Those at 4 K and room temperature are given in Table 2, and those at intermediate temperatures are disclosed in the Supporting Information (Tables S1–S4). For comparison, these measurements were also conducted for bis(pyridyl) derivative **9b**, the brightest fluorescent phosphole sulfide (see also Figure 6), which has the longest lifetime over the entire temperature range.



Figure 6. Lifetimes for phospholes 10a (\diamond), 10b (\times) and 10c (+), and phosphole sulfide 9b (\bigcirc).

The radiative decay constant $(k_{\rm F})$ of the emissive substance can be determined from the room-temperature value of τ and $\Phi_{\rm F}$ according to Equation (1). As $k_{\rm F}$ is temperature-independent, the non-radiative decay constant $(k_{\rm nr})$ can be computed at all temperatures using Equation (2) (see Supporting Information, Tables S1–S4).

$$\tau = \Phi_{\rm F}/k_{\rm F} \text{ (at r.t.)} \tag{1}$$

$$\Phi_{\rm F} = (k_{\rm nr} + k_{\rm F})/k_{\rm F} \tag{2}$$

Since τ and k_{nr} are of similar magnitude for the phosphole sulfide **9b** and the phospholes **10a–c**, the low quantum yield for **9a–c** cannot be explained by a rapid nonradiative decay of the S_1 to the S_0 state (internal conversion). A more plausible explanation is a high rate of intersystem crossing to a triplet state for the phosphole sulfides, which may be caused by the presence of the "heavy atom" sulfur. The small fraction of molecules that decay to the vibrational ground state of the S_1 state must then be presumed to fluoresce just as efficiently as the corresponding σ^3 -phospholes. However, because no phosphorescence is detected, we conclude that the triplet state decays nonradiatively.

It is evident that the influence of the aromatic end-group on the optical properties is subtle and less pronounced than in related systems in which the (hetero)aromatic rings are directly attached in the 2- and 5-position at the phosphole ring. Incorporation of cross-conjugation over the phenyl rings of the extended π -systems of **9a–c** and **10a–c** slightly reduces the efficient interaction with the phospholes as compared to the interaction with directly attached (hetero)aromatic substituents.

Cyclic Voltammetry

Phosphole sulfides **9a–c** can be reduced between -1.91 V and -2.04 V vs. Fc/Fc⁺ (Table 3), which is consistent with the fairly low-lying LUMO of the phosphole-based π -systems. On the other hand, no anodic waves were detected below +1.0 V. Phospholes **10a–c** exhibit slightly more negative cathodic waves between -2.25 V and -2.35 V vs. Fc/Fc⁺ (Table 3), in line with the DFT data (see below, Figure 9). Notably, the cathodic potentials of the extended π -systems **10a–c** reveal that their LUMO levels are still significantly

lower-lying compared to those of their less extended counterparts 2,5-diphenylphosphole ($E^{0'} = -2.88$ V) and 2,5-dithienylphosphole $(E^{0'} = -2.45 \text{ V})$.^[6a] The reductions of phosphole sulfides 9 are fully reversible at room temperature, but only partly reversible for the free phospholes 10 $(i_{p,a}/i_{p,c} < 1 \text{ at } v = 100 \text{ mV s}^{-1})$. The subsequent reduction of the radical anions $[9a-c]^-$ to the corresponding dianions is totally irreversible and affected by weak adsorption (Table 3). This second reduction was also observed for the short-lived radical anions of phosphole sulfides 10a and **10c.** Exemplary for this redox behavior is the cyclic voltammogram of bis(phenyl)phosphole sulfide 9a (Figure 7), in which the solid line represents the reversible first reduction and the dotted line represents the irreversible second cathodic wave. Notably, oxidation of a secondary species formed by degradation of unstable $[9a]^{2-}$ is perceptible at -1.02 V (vs. Fc/Fc⁺) on the reverse anodic scan. For $[10a]^{2-}$ the corresponding anodic wave is shifted to -0.75 V. Lowering the temperature enhances the stability of the radical anions and dianions, but it also results in a decreased rate of electron transfer, thus giving quasi-reversible reduction waves for both the phosphole sulfides 9a-c and the free phospholes 10a-c (see Supporting Information, Figure S1 for the cyclic voltammogram of **9a** at 223 K).

Table 3. Electrochemical data^[a] for phosphole sulfides 9a-c and phospholes 10a-c.

	9a	9b	9c	10a	10b	10c
$ \frac{E_{1/2} (1) [V]}{E_{m,n} (2) [V]^{[d]}} $	-1.91 ^[b] -2.24	-1.93 ^[b] -2.35	-2.04 ^[b] -2.49	-2.25 ^[c] -2.62	-2.33 ^[c]	-2.35 ^[c]

[a] Experimental conditions: 10^{-1} M Bu₄NPF₆ in C₃H₇CN, Pt microdisc electrode, scan rate = 100 mV s⁻¹, T = 293 K. [b] Fully reversible first reduction, potentials given vs. Fc/Fc⁺. [c] Irreversible cathodic wave ($i_{p,a}/i_{p,c} < 1$), potential vs. Fc/Fc⁺. [d] Irreversible second reduction, cathodic peak potential vs. Fc/Fc⁺. [e] Not recorded.



Figure 7. Cyclic voltammogram of bis(phenyl)phosphole sulfide 9a, showing the reversible first reduction to $[9a]^-$ (solid) and the irreversible second reduction to $[9a]^{2-}$ (dashed), recorded at r.t. in C₃H₇CN at a Pt microdisc electrode (scan rate = 100 mV s⁻¹).

UV/Vis Spectroelectrochemistry

The nature of the pyridyl-substituted radical anion [9b] was further examined by UV/Vis spectroelectrochemistry at room temperature (Figure 8). In the course of the cathodic

conversion of bis(pyridyl)phosphole sulfide **9b** to [**9b**]⁻ a new low-energy absorption band appeared gradually at $\lambda_{max} = 609$ nm [see inset (a) in Figure 8]. The stability of [**9b**]⁻ on the time scale of the experiment has been indicated by the presence of an isosbestic point at ca. 410 nm. When the electrode potential was further shifted to more negative values corresponding to the second reduction, i.e. below -2.35 V, the radical anion converted to an unidentified secondary reduction product, exhibiting an absorption maximum at $\lambda_{max} = 377$ nm [see inset (b) in Figure 8].



Figure 8. UV/Vis absorption spectral changes accompanying the stepwise reduction of bis(pyridyl)phosphole sulfide **9b** to [**9a** $]^-$ and [**9a** $]^2^-$ within an OTTLE cell (continuous scanning at 2 mV s⁻¹). (a) Spectra 1–8 show the isosbestic appearance of a new band at 609 nm belonging to stable [**9a** $]^-$. (b) Spectra 8–15 show the appearance of a new band at 377 nm belonging most likely to a secondary reduction product arising from highly unstable [**9a** $]^2^-$.

In accordance with the irreversible nature of the electrochemical reduction of bis(pyridyl)phosphole **10b** at ambient temperature (see above), the corresponding radical anion was not observed in the course of in situ spectroelectrochemistry.

DFT Calculations

To assist in elucidating the electronic structure of the phosphole-containing π -systems **9a–c** and **10a–c**, their optimized structures and frontier orbitals were computed by symmetry-restricted PCM-TDDFT calculations.^[15] The geometry with both π -conjugated arms pointing "downwards" and the triazole nitrogen atoms pointing out (as depicted in Scheme 2 and Figure 9) belongs to the most stable conformer of all six π -systems. The frontier orbitals of the π -systems are depicted together with the corresponding relative energies in Figure 9.

The LUMOs of all the π -systems are almost identical in nature, irrespective of the aromatic end-group, exhibiting conjugation between the phosphole ring and the adjacent phenyl rings. Some mixing of the $\sigma^*(PS)$ orbital into the π^* orbital results in a lowering in energy of the phosphole sulfide based LUMOs. Also, the energies of the HOMOs of the phosphole compounds (**10a–c**) are slightly higher in energy compared to the phosphole sulfide compounds (**9a–c**). Some variation occurs in the shape of the HOMOs, as thienyl-substituted **9c** exhibits a HOMO, which is delocalized over the entire molecule, as opposed to the other π -systems.

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Figure 9. Frontier orbitals (LUMOs top and HOMOs bottom) of phosphole sulfide based π -systems **9a–c** and phosphole based π -systems **10a–c**, with corresponding relative energies and corresponding HOMO–LUMO gap ($\Delta E_{\rm HL}$) in eV, calculated with PCM-TDDFT at CAM-B3LYP/cc-pVTZ.

This leads to significant charge-transfer for this specific compound, which may relate to the observed very low quantum yield of $\Phi_{\rm F} = 0.0071$. Also some spreading of the HOMO to the triazole rings and aromatic end-groups, although to a lesser extent, is observed for **9a**, **9b** and **10c**. Several occupied *p*-orbitals are close in energy and type of aromatic end-group has some influence on the extent to which they contribute to the HOMO.

The calculated HOMO–LUMO gaps ($\Delta E_{\rm HL}$) of the λ^3 phosphole π -systems **10a–c** are significantly larger than those of the sulfur-protected ones (Figure 9), which is in accordance with the absorption spectra. However, the emission spectra show an opposite effect, as the values for $\lambda_{\rm em}$ of the λ^3 -phospholes are shifted towards lower energies with respect to those of the phosphole sulfides. This discrepancy may be explained by a higher degree of relaxation for the excited states of the free phospholes. Variations in absorption and emission maxima, caused by the presence of different aromatic end-groups, are not reflected in the calculated $\Delta E_{\rm HL}$ values of the phosphole-based π -systems.

The singlet vertical excitation energies were calculated with linear response PCM-TDDFT.^[15] The lowest-lying singlet vertical excitation energy and oscillator strengths along with the main excitation configuration of the phospholecontaining π -systems are listed in Table 4. The calculated absorption maxima of phosphole sulfides [$\lambda_{abs}(9a-c) = 395-$ 411 nm] and phospholes [$\lambda_{abs}(10a-c) = 362-364$ nm] correspond very well to the experimentally obtained ones $[\lambda_{abs}(9a-c) = 382-385 \text{ nm}; \lambda_{abs}(10a-c) = 355-356 \text{ nm}].$ The excitations of the compounds are mainly related to transitions involving the two frontier orbitals (HOMO and LUMO), except for compound 9c, where also the HOMO-2 plays an important role in the excitation, having a contribution of 40%. The HOMO-2 orbital of 9c is similar in shape and 0.21 eV lower in energy, compared to the corresponding HOMO. The lowest-energy transitions can all be assigned to be of $\pi \to \pi^*$ character. For the phosphole sulfides (9a-c) a second transition can be allocated to be of $n \rightarrow \pi^*$ type from the sulfur lone pair into the empty π orbital.

Table 4. PCM-TDDFT analysis of phosphole sulfides 9a-c and phospholes 10a-c.

	$\lambda_{abs}^{[a]}$ [eV]	λ_{abs} [nm]	<i>f</i> ^[b]	Configuration ^[c]	Transition
9a	3.14	395	0.4555	$HOMO \rightarrow LUMO$ (80%)	$\pi \to \pi^*$
	3.68	337	0.1315	HOMO-3 \rightarrow LUMO (90%)	$n \to \pi^*$
9b	3.03	409	0.5406	$HOMO \rightarrow LUMO$ (92%)	$\pi \to \pi^*$
	3.66	338	0.1024	$HOMO-3 \rightarrow LUMO$ (92%)	$n \to \pi^*$
9c	3.02	411	0.5439	HOMO \rightarrow LUMO (54%)	$\pi \to \pi^*$
				HOMO-2 \rightarrow LUMO (40%)	
	3.66	339	0.0934	HOMO-3 \rightarrow LUMO (92%)	$n \to \pi^*$
10a	3.41	364	0.6574	$HOMO \rightarrow LUMO$ (93%)	$\pi \to \pi^*$
10b	3.43	362	0.6859	$HOMO \rightarrow LUMO$ (94%)	$\pi \to \pi^*$
10c	3.42	363	0.6849	$HOMO \rightarrow LUMO$ (88%)	$\pi \to \pi^*$

[a] The calculated excitation energies of the phosphole sulfide compounds **9a–c** and the phosphole compounds **10a–c** are underestimated by an average of 10–30 nm. [b] Oscillator strength. [c] Dominant orbital transitions.

In summary, these results demonstrate clearly that the influence of the aromatic end-groups is subtle but not negligible. The nature of the group at the terminal position has some influence on the shape of the HOMO and, as such, determines the amount of charge transfer occurring during excitation. Also, some tuning of the emission wavelength is accomplished, which exerts an influence on the HOMO– LUMO gap. Such fine-tuning of the photophysical properties is indeed observed, despite the presence of cross-conjugation between both triazole moieties and the central phosphole ring.

Conclusions

We have synthesized a bifunctional 2,5-diphenylphosphole-based π -system with functional moieties that effectively extend the π -conjugated framework. Bis(azidophenyl)phosphole sulfide building block **8**, obtained in 31% yield in a multi-step reaction sequence, was efficiently functionalized using the copper-catalyzed Huisgen 1,3-dipolar cycloaddition to provide extended π -systems with phenyltriazolyl (**9a**), pyridyltriazolyl (**9b**) and thienyltriazolyl (**9c**) end-groups and the corresponding sulfur-free $\lambda^3 \sigma^3$ -phosphorus-based **10a–c**.

The π -systems **10a**–c fluoresce efficiently in the bluegreen region ($\lambda_{\rm em} = 460-469$ nm; $\Phi_{\rm F} = 0.13-0.31$), which represents a significant bathochromic shift and strongly increased luminescence intensity compared to their phosphole sulfide based analogues **9a–c** ($\lambda_{\rm em} = 414-416$ nm; $\Phi_{\rm F} =$ 0.00071–0.0036). The origin of the low fluorescence quantum yields of the phosphole sulfide based π -systems has been attributed to intersystem crossing to a non-radiatively



decaying triplet state. The π -systems of **9a–c** and **10a–c** are easily reducible, and the electrogenerated radical anions of the pyridyl-substituted phosphole sulfide **9b** could be identified spectroscopically at room temperature [$\lambda_{abs}(\mathbf{9b}^{-}) = 609 \text{ nm}$].

The nature of the (aromatic) end-group determines to some extent which *p*-orbitals contribute to the HOMO of the π -system. The TDDFT calculations reveal that some fine-tuning of the photophysical properties of the extended π -systems is achieved by determining the extent of chargetransfer occurring during excitation, which has a subtle effect on the shape and location of the HOMO and on the size of the HOMO–LUMO gap.

Their intense fluorescence, the relative stability of their radical anions, and their tunability make the λ^3 -phospholebased π -systems **10a**-c potential candidates for incorporation into electronic devices such as OLEDs. Moreover, use of the bis(azidophenyl)phosphole sulfide building block **8** in the so-called click reaction may give access to diverse fluorescent probes suitable in solid-state, biomolecular, and enzymatic systems.

Experimental Section

General Remarks: All reactions were carried out under nitrogen using standard Schlenk techniques and dry solvents, unless stated otherwise. THF and Et₂O were distilled from Na/benzophenone, NEt₃ from CaH₂, CH₂Cl₂ from CaCl₂ and toluene from Na. 2-Ethynyl-thiophene^[16] and P(NMe₂)₃^[17] were prepared according to literature procedures and were kept as stock solutions (0.15 M in CH₂Cl₂ and 1.5 M in THF respectively). NMR measurements were performed with a Bruker Avance 250 or a Bruker Avance 400 spectrometer. NMR chemical shifts were externally referenced to SiMe₄ (¹H and ¹³C) or 85% H_3PO_4 (³¹P). Atom numbering of the 2,5diarylphosphole system is according to Figure 2. IR spectra were recorded with a Mattson-6030 Galaxy FT-IR spectrophotometer (KBr) or a Shimadzu FTIR-8400s spectrophotometer (neat), and high-resolution mass spectra were measured using a Finnigan Mat 900 mass spectrometer operating at an ionization potential of 70 eV (EI) or a JEOL JMS SX/SX 102A four-sector mass spectrometer, equipped with a Xenon primary atom beam, utilizing a 3-nitrobenzyl (3-NOBA) matrix (FAB). Melting points were measured with a Stuart Scientific SMP3 melting point apparatus in unsealed capillaries and are uncorrected. UV/Vis absorption spectra were recorded at room temperature with a Carey 300 UV/Vis spectrophotometer and room temperature fluorescence spectra with a Perkin-Elmer LS50-B spectrofluorimeter, using 10 mm quartz cuvettes. Spectra were recorded with a scan speed of 200 nm/min, using a spectral width of 5 nm for both excitation and emission. Quantum yields were determined in cyclohexane as 10⁻⁴ M solutions for phosphole sulfides 9a-c and as 10^{-7} M solutions for phospholes 10a-c, using perylene as standard ($\Phi_{\rm F} = 94\%$). Temperature-dependent luminescence life-time measurements were performed with an Edinburgh FLS 920 spectrofluorimeter using timecorrelated photon counting under pulsed excitation at 375 nm with an EPL375 picosecond diode laser. The temperature was varied using an Oxford Instruments Optistat CF liquid helium flow cryostat in combination with an ITC temperature controller. The sample solution was inserted in a homemade quartz cuvette of ca. 1 cm diameter. Conventional cyclic voltammetric experiments were performed using a computer-controlled EG&G PAR 283 potentiostat

connected to an air-tight single-compartment cell containing a Pt microdisc (0.14 mm² surface) working electrode (polished freshly between scans with a 0.25 µm grain diamond paste), a Pt wire auxiliary electrode and an Ag wire pseudoreference electrode calibrated with ferrocene as an internal standard. The compounds were studied as 10⁻³ M solutions in dry C₃H₇CN, distilled freshly from CaH₂. Bu₄NPF₆ (Aldrich) was recrystallized twice from absolute ethanol and dried under vacuum at 80 °C overnight prior to using it as the 10⁻¹ M supporting electrolyte. UV/Vis absorption spectroelectrochemical experiments were carried out with an optically transparent thin-layer electrochemical (OTTLE) cell equipped with CaF₂ windows.^[18] The potential of the Pt minigrid (32 wires per cm) working electrode was controlled with a PA4 potentiostat (Laboratory Devices, Polná, Czech Republic). The potential scan rate was 2 mV s⁻¹. The UV/Vis absorption spectra were recorded with an HP8453 diode array spectrophotometer in intervals of a few seconds at continuous potential sweep.

1,8-Bis(3-bromophenyl)octa-1,7-diyne (4): To a solution of 1-bromo-3-iodobenzene (3.18 mL, 25.0 mmol, 2.0 equiv.) and octa-1,7-divne (1.69 mL, 12.75 mmol, 1.02 equiv.) in NEt₃ (30 mL) and THF (100 mL), Pd(OAc)₂ (56 mg, 0.25 mmol, 2%), PPh₃ (131 mg, 0.50 mmol, 4%) and CuI (95 mg, 0.50 mmol, 4%) were added, and the mixture was stirred at room temp. for 16 h. The dark yellow turbid solution was diluted with pentane and washed with 0.5 M HCl (aq.), H₂O, 5% NaHCO₃ (aq.) and H₂O. The organic layer was dried with MgSO₄, filtered, and the solvents were removed in vacuo. The dark red residue was purified by column chromatography on silica gel eluting with hexane/CH₂Cl₂, 10:0 to 7:3 [$R_{\rm F}$ (3:1) = 0.32], which afforded **4** as white semi-crystalline solid (5.08 g, 12.2 mmol, 98%). M.p. 41.7-42.7 °C. ¹H NMR (250.13 MHz, CDCl₃): δ = 7.55 (s, 2 H, ArH²), 7.40 (d, ³J_{HH} = 8.0 Hz, 2 H, Ar H^4), 7.32 (d, ${}^{3}J_{HH}$ = 7.8 Hz, 2 H, Ar H^6), 7.14 (t, ${}^{3}J_{HH}$ = 7.8 Hz, 2 H, Ar H^5), 2.48 (br. s, 4 H, =C-C H_2 -C H_2 -), 1.78 (br. s, 4 H, =C-CH₂-CH₂-) ppm. ¹³C NMR (62.90 MHz, CDCl₃): δ = 134.8 (s, ArC²), 131.2 (s, ArC⁴), 130.5 (s, ArC⁶), 130.0 (s, ArC⁵), 126.4 (s, ArC^{1} , 122.4 (s, ArC^{3}), 91.7 (s, $Ar-C \equiv C$ -), 80.0 (s, $Ar-C \equiv C$ -), 28.1 $(s, \equiv C-CH_2-CH_2-), 19.4 (s, \equiv C-CH_2-CH_2-) \text{ ppm. HRMS (EI):}$ calcd. for $C_{20}H_{16}Br_2$ [M] 413.9619; found 413.9614; m/z (%) = 418 (12) $[M]^+$ (⁸¹Br₂), 416 (23) $[M]^+$ (⁸¹Br⁷⁹Br), 414 (12) $[M]^+$ (⁷⁹Br₂). IR (KBr): $\tilde{v} = 2943$ (w), 1588 (m), 1550 (m), 1470 (m), 1402 (w), 1324 (w), 1217 (w), 1073 (w), 993 (w), 869 (w), 784 (s), 722 (w), 680 (m), 436 (w) cm⁻¹. UV/Vis (CH₂Cl₂): $\lambda_{abs} = 255 \text{ nm}$ ($\varepsilon =$ $2.11 \times 10^4 \text{ m}^{-1} \text{ cm}^{-1}$).

1,8-Bis{3-[(diphenylmethylene)amino]phenyl}octa-1,7-divne (5): Compound 4 (2.08 g, 5.00 mmol) was dissolved in Et₂O (20 mL), and the solvent was removed under reduced pressure. This was repeated two more times to remove traces of water; 4 was then dissolved in toluene (150 mL), and benzophenone imine (2.00 mL, 12.0 mmol, 2.4 equiv.), Pd2dba3 (46 mg, 0.050 mmol, 1%), BINAP (93 mg, 0.15 mmol, 3%) and NaOtBu (1.35 g, 14.0 mmol, 2.8 equiv.) were added. The black reaction mixture was stirred at 80 °C for 48 h. The colour changed to yellow turbid, and the reaction mixture was diluted with pentane and washed with H₂O and 0.25 M HCl (aq.). The organic layer was dried with MgSO₄, filtered, and the solvents were removed in vacuo. The dark orange residue was purified by column chromatography on silica gel eluting with hexane/EtOAc, 9:1 ($R_{\rm F} = 0.30$) to obtain 5 as a slightly yellow powder (3.08 g, 5.00 mmol, 100%). M.p. 71.8-72.4 °C. ¹H NMR (400.13 MHz, CDCl₃): δ = 7.66 (d, ${}^{3}J_{HH}$ = 7.3 Hz, 4 H, *o-Z-PhH*), 7.39 (tt, ${}^{3}J_{HH} = 7.3$, ${}^{4}J_{HH} = 1.8$ Hz, 2 H, *p-Z-PhH*), 7.32 (t, ${}^{3}J_{HH}$ = 7.3 Hz, 4 H, *m*-*Z*-Ph*H*), 7.15–7.20 (m, 6 H, *m*-*E*-Ph*H*, *p*-*E*-Ph*H*), 7.01–7.05 (m, 4 H, *o*-*E*-Ph*H*), 6.94 (t, ${}^{3}J_{HH} = 7.7$ Hz, 2 H, Ar H^{5}), 6.88 (dt, ${}^{3}J_{HH} = 7.7$, ${}^{4}J_{HH} = 1.6$ Hz, 2 H, Ar H^{6}), 6.76 (t, ${}^{4}J_{HH} =$

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1.6 Hz, 2 H, Ar H^2), 6.48 (ddd, ${}^{3}J_{HH} = 7.7$, ${}^{4}J_{HH} = 1.6$, ${}^{4}J_{HH} =$ 1.3 Hz, 2 H, Ar H^4), 2.34 (m, 4 H, =C-C H_2 -C H_2 -), 1.64 (m, 4 H, \equiv C-CH₂-CH₂-) ppm. ¹³C NMR (62.90 MHz, CDCl₃): δ = 169.0 (s, Ph₂C=N-), 151.6 (s, ArC³), 139.9 (s, ipso-Z-PhC), 136.3 (s, ipso-E-PhC), 131.2 (s, p-Z-PhC), 129.8 (s, o-E-PhC), 129.7 (s, o-Z-PhC), 129.1 (s, p-E-PhC), 128.7 (s, ArC⁵), 128.6 (s, m-Z-PhC), 128.4 (s, *m*-*E*-Ph*C*), 126.8 (s, Ar*C*⁶), 124.50 (s, Ar*C*²), 124.47 (s, Ar*C*¹), 120.6 (s, ArC⁴), 89.9 (s, Ar–C=C–), 81.3 (s, Ar–C=C–), 28.2 (s, =C– CH_2-CH_2-), 19.4 (s, $\equiv C-CH_2-CH_2-$) ppm. In the ¹H and ¹³C NMR spectroscopic data, the imine phenyl ring pointing towards the phenyloctadiyne moiety is labeled Z, and the phenyl ring pointing away is labeled E. HRMS (EI): calcd. for C₄₆H₃₇N₂ [M] 617.2957, found 617.2960; m/z (%) = 617 (100) [M + H]⁺, 616 (77) [M]⁺, 539 (16) $[M - Ph]^+$. IR (neat): $\tilde{v} = 3057$ (w, C_{Ar}-H), 2938 (w, CH₂), 2861 (w, CH₂), 1585 (s, N = H), 1570 (s), 1491 (w), 1474 (m), 1447 (m), 1418 (w), 1314 (w), 1302 (w), 1296 (w), 1254 (m), 1186 (m), 1134 (m), 1074 (w), 966 (s), 949 (m), 926 (m), 874 (m) cm⁻¹. UV/ Vis (CH₂Cl₂): $\lambda_{abs} = 254$ ($\epsilon = 7.35 \times 10^4 \text{ m}^{-1} \text{ cm}^{-1}$), 336 nm ($\epsilon =$ $5.86 \times 10^3 \text{ m}^{-1} \text{ cm}^{-1}$).

2,5-Bis{3-[(diphenylmethylene)amino]phenyl}-1-phenyl-1-thiooxophosphole (6): Compound 5 (1.07 g, 1.74 mmol) was dissolved in Et₂O (15 mL) and the solvent removed under reduced pressure. This was repeated two more times to remove traces of water. In a separate Schlenk vessel, ZrCp₂Cl₂ (508 mg, 1.74 mmol, 1.0 equiv.) was suspended in THF (25 mL). At -78 °C, nBuLi (1.6 M in hexane, 2.28 mL, 3.65 mmol, 2.1 equiv.) was added dropwise to the mixture of ZrCp₂Cl₂ in THF over 20 min. After stirring at -78 °C for 30 min, a solution of 5 in THF (30 mL) was added dropwise to the yellow reaction mixture of ZrCp₂ over 40 min. The reaction mixture was slowly warmed to room temperature, during which the reaction mixture turned dark red, indicating the formation of the zirconocyclopentadiene species. After stirring at room temperature for 3 h, the reaction mixture was cooled to 0 °C, and CuCl (361 mg, 3.65 mmol, 2.1 equiv.) was added. Stirring was continued at 0 °C for 30 min, after which PhPCl₂ (236 µL, 1.74 mmol, 1.0 equiv.) was added dropwise at 0 °C over 15 min. The dark reaction mixture was slowly warmed to room temperature with continued stirring for 16 h. Then, S₈ (89.1 mg, 347 µmol, 0.2 equiv.) was added, and the clear yellow reaction mixture was stirred for another 5 h. The solvent was removed and the dry residue redissolved in CHCl₃, which was washed extensively with H₂O. The combined H₂O layers were extracted with additional CHCl₃, and the combined organic layers were dried with MgSO₄, filtered, and the solvent was removed in vacuo. The green residue was purified by column chromatography on silica gel eluting with pentane/EtOAc, 9:1 to 2:1 [$R_{\rm F}$ (9:1) = 0.08] to obtain 6 as a yellow powder (1.04 g, 1.37 mmol, 79%). M.p. 154.8-155.2 °C (decompos.), 165.7-165.9 °C (melt.). ¹H NMR (400.13 MHz, CDCl₃): δ = 7.69 (d, ³J_{HH} = 7.2 Hz, 4 H, o-Z-PhH), 7.63–7.68 (m, ${}^{3}J_{HP}$ = 13.7 Hz, 2 H, o-PPh*H*); 7.41–7.46 (m, ${}^{4}J_{HH}$ = 1.9 Hz, 1 H, *p*-PPh*H*), 7.45 (t, ${}^{3}J_{HH}$ = 7.2 Hz, 4 H, *p*-*Z*-Ph*H*), 7.37 (t, ${}^{3}J_{HH}$ = 7.2 Hz, 4 H, *m*-*Z*-Ph*H*), 7.30–7.35 (m, 2 H, *m*-PPh*H*), 7.23 (t, ${}^{3}J_{HH}$ = 7.3 Hz, 2 H, *p*-*E*-PhH), 7.19 (t, ${}^{3}J_{HH} = 7.3 \text{ Hz}$, 4 H, *m*-*E*-PhH), 7.04 (t, ${}^{3}J_{HH} =$ 7.8 Hz, 2 H, Ar H^5), 7.03 (d, ${}^{3}J_{HH} = 7.3$ Hz, 4 H, *o-E-PhH*); 6.99 (dd, ${}^{3}J_{HH} = 7.8$, ${}^{4}J_{HH} = 0.8$ Hz, 2 H, Ar H^{6}), 6.65 (d, ${}^{3}J_{HH} = 7.8$ Hz, 2 H, Ar H^4), 6.58 (s, 2 H, Ar H^2), 2.32 (dd, ${}^2J_{HH}$ = 18.0, ${}^4J_{HP}$ = 3.1 Hz, 2 H, C_q-CH₂-), 2.23 (dd, ${}^{2}J_{HH}$ = 18.0, ${}^{4}J_{HP}$ = 3.1 Hz, 2 H, C_q-CH₂-), 1.56 (br. s, 4 H, -CH₂-CH₂-) ppm. ¹³C NMR (62.90 MHz, CDCl₃): δ = 168.3 (s, Ph₂C=N-), 151.1 (s, ArC³), 147.8 (d, ${}^{2}J_{CP}$ = 23.3 Hz, PC=C), 139.5 (s, *ipso-Z-PhC*), 135.9 (s, *ipso-E-PhC*), 133.5 (d, ${}^{1}J_{CP}$ = 92.4 Hz, PC=C), 132.9 (s, ArC¹), 131.4 (d, ${}^{4}J_{CP} = 2.5$ Hz, p-PPh), 130.59 (s, p-Z-PhC), 130.57 (d, ${}^{3}J_{CP} = 11.0 \text{ Hz}, \text{ m-PPh}), 129.5 \text{ (s, } o-E-PhC), 129.2 \text{ (s, } o-Z-PhC),$

128.43 (d, ${}^{2}J_{CP}$ = 12.7 Hz, *o*-PPh), 128.41 (d, ${}^{4}J_{CP}$ = 1.3 Hz, ArC⁵), 128.3 (s, *p*-*E*-Ph*C*), 128.2 (d, ${}^{1}J_{CP}$ = 73.5 Hz, *ipso*-PPh), 128.0 (s, m-Z-PhC), 127.8 (s, m-E-PhC), 123.6 (d, ${}^{3}J_{CP} = 3.8$ Hz, ArC⁶), 121.2 (d, ${}^{3}J_{CP} = 6.8 \text{ Hz}$, ArC²), 120.5 (s, ArC⁴), 27.3 (d, ${}^{3}J_{CP} =$ 13.2 Hz, C_q-CH₂-CH₂-), 22.4 (s, C_q-CH₂-CH₂-) ppm. ³¹P NMR (CDCl₃; 101.25 MHz): δ = 53.5 (s) ppm. In the ¹H and ¹³C NMR spectroscopic data, the imine-phenyl ring pointing towards the phenyloctadiyne moiety is labeled Z, and the phenyl ring pointing away is labeled E. HRMS (EI): calcd. for C₅₂H₄₂N₂PS [M + H] 757.2806, found 751.2811; m/z (%) = 757 (100) [M + H]⁺, 756 (39) $[M]^+$, 679 (5) $[M - Ph]^+$. IR (neat): $\tilde{v} = 3052$ (w), 2943 (w), 2868 (w), 1613 (w), 1587 (m), 1572 (s), 1476 (w), 1445 (m), 1317 (m), 1287 (m), 1142 (w), 1104 (m), 1075 (w), 1026 (w), 955 (m), 892 (w), 784 (m), 765 (m), 746 (m), 697 (s), 662 (s) cm⁻¹. UV/Vis (CH₂Cl₂): $\lambda_{\rm abs} = 229 \ (\varepsilon = 5.08 \times 10^4 \, {\rm M}^{-1} \, {\rm cm}^{-1}), \ 248 \ (\varepsilon = 5.47 \times 10^4 \, {\rm M}^{-1} \, {\rm cm}^{-1}),$ 336 nm ($\varepsilon = 1.35 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$).

2,5-Bis(3-aminophenyl)-1-phenyl-1-thiooxophosphole (7): 0.5 M HCl (aq. 20 mL, 5 equiv.) was added to a solution of 6 (1.44 g, 1.90 mmol) in wet THF (50 mL). The reaction mixture was refluxed for 3 h, subsequently diluted with Et₂O and washed with H₂O and 5% NaHCO₃ (aq.). The organic layer was dried with MgSO₄, filtered, and the solvents were removed in vacuo. The yellow residue was purified by column chromatography on Al₂O₃ eluting with hexane/EtOAc, 4:1 to 0:1 [$R_{\rm F}$ (EtOAc) = 0.91] to remove benzophenone, which afforded 7 as a yellow foam (530 mg, 1.24 mmol, 65%). M.p. 80.3-80.6 °C (decompos.); 96.2-97.5 °C (melt.). ¹H NMR (400.13 MHz, CDCl₃): $\delta = 7.82$ (ddd, ³J_{HP} = 13.6, ${}^{3}J_{HH} = 7.6$, ${}^{4}J_{HH} = 1.5$ Hz, 2 H, *o*-PPh*H*), 7.36–7.47 (m, 3 H, *m*-PPh*H*, *p*-PPh*H*), 7.05 (t, ${}^{3}J_{HH} = 7.8$ Hz, 2 H, Ar H^{5}), 6.75 (s, 2 H, Ar H^2), 6.64 (d, ${}^{3}J_{HH}$ = 7.6 Hz, 2 H, Ar H^6), 6.57 (dd, ${}^{3}J_{HH}$ = 8.0, ${}^{4}J_{HH}$ = 1.1 Hz, 2 H, Ar H^{4}), 3.51 (br. s, 4 H, NH₂), 2.77 (br. s, 4 H, C_q-CH₂-CH₂), 1.76 (br. s, 4 H, C_q-CH₂-CH₂) ppm. ¹³C NMR (62.90 MHz, CDCl₃): δ = 147.9 (d, ² J_{CP} = 23.5 Hz, PC=*C*), 146.0 (s, ArC³), 133.9 (d, ${}^{1}J_{CP}$ = 66.6 Hz, PC=C), 133.4 (d, ${}^{2}J_{CP}$ = 1.4 Hz, Ar C^1), 131.4 (d, ${}^4J_{CP}$ = 3.0 Hz, *p*-PPh), 130.6 (d, ${}^3J_{CP}$ = 11.4 Hz, *m*-PPh), 129.0 (s, ArC⁵), 128.5 (d, ${}^{2}J_{CP}$ = 12.4 Hz, *o*-PPh), 128.2 (d, ${}^{1}J_{CP}$ = 73.4 Hz, *ipso*-PPh), 119.4 (d, ${}^{3}J_{CP}$ = 5.3 Hz, ArC⁶), 115.5 (d, ${}^{3}J_{CP}$ = 4.9 Hz, ArC²), 114.6 (d, ${}^{5}J_{CP}$ = 1.1 Hz, ArC⁴), 27.8 (d, ${}^{3}J_{CP} = 13.4 \text{ Hz}, C_{q}-CH_{2}-CH_{2}-), 22.6 \text{ (s, } C_{q}-CH_{2}-CH_{2}) \text{ ppm. } {}^{31}\text{P}$ NMR (101.25 MHz, CDCl₃): δ = 53.9 (s) ppm. HRMS (EI): calcd. for C₂₆H₂₆N₂PS [M + H] 428.1554, found 429.1548; m/z (%) = 429 (100) $[M + H]^+$, 428 (54) $[M]^+$. IR (neat): $\tilde{v} = 2923$ (w), 2858 (w), 1614 (m), 1596 (m), 1580 (m), 1487 (m), 1435 (m), 1303 (m), 1228 (w), 1166 (w), 1095 (m), 1025 (w), 997 (w), 907 (w), 867 (w), 776 (m), 744 (m), 716 (s), 689 (s), 668 (s) cm⁻¹. UV/Vis (CH₂Cl₂): λ_{abs} = 230 (ε = 1.40×10⁴ M⁻¹ cm⁻¹), 278 (sh, ε = 5.80×10³ M⁻¹ cm⁻¹), 333 nm ($\varepsilon = 4.40 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$).

2,5-Bis(3-azidophenyl)-1-phenyl-1-thiooxophosphole (8): 0.5 M HCl (aq. 4 mL, 4.0 equiv.) was added slowly to a solution of 7 (230 mg, 537 µmol) in wet THF (6 mL) at -5 °C. To this viscous solution, NaNO₂ (88.9 mg, 1.29 mmol, 2.4 equiv.) in H₂O (2 mL) was added dropwise over 7 min and stirring was continued for 20 min. Then, urea (10 mg, 0.17 mmol, 0.3 equiv.) was added to destroy the excess nitrous acid. The reaction mixture was carefully poured into a solution of NaN₃ (140 mg, 2.15 mmol, 4.0 equiv.) and NaOAc (264 mg, 3.22 mmol, 6 equiv.) in H₂O (5 mL) at -5 °C, and rinsed with THF (2 mL). Stirring of the orange viscous suspension was continued at -5 °C for 2 h, after which the reaction mixture was diluted with Et₂O and the organic layer washed with H₂O. The organic layer was dried with MgSO₄, filtered, and the solvent removed in vacuo. The orange residue was purified by column chromatography on silica gel eluting with hexane/EtOAc, 9:1 to 1:1 [$R_{\rm F}$ (9:1) = 0.33] to obtain 8 as a yellow powder (160 mg, 333 µmol, 62%). Cubic crys-



tals of 8, suitable for X-ray analysis, were grown by slow cooling of a hexane solution. M.p. 110.4–110.9 °C. ¹H NMR (250.13 MHz, CDCl₃): δ = 7.84 (dd, ${}^{3}J_{HP}$ = 13.8, ${}^{3}J_{HH}$ = 6.8 Hz, 2 H, *o*-PPh*H*), 7.41–7.55 (m, 3 H, *m*-PPh*H*, *p*-PPh*H*), 7.29 (t, ${}^{3}J_{HH}$ = 8.0 Hz, 2 H, ArH^{5}), 7.13 (d, ${}^{3}J_{HH}$ = 8.0 Hz, 2 H, ArH^{6}), 6.96 (s, 2 H, ArH^{2}), 6.93 (d, ${}^{3}J_{HH} = 8.0 \text{ Hz}$, 2 H, Ar H^{4}), 2.79 (br. s, 4 H, C_q-C H_{2} -CH₂), 1.81 (br. s, 4 H, C_q-CH₂-CH₂) ppm. ¹³C NMR (62.90 MHz, CDCl₃): $\delta = 148.7$ (d, ${}^{2}J_{CP} = 22.5$ Hz, PC=C), 140.1 (s, ArC³), 134.3 (s, Ar C^1), 133.6 (d, ${}^1J_{CP}$ = 68.1 Hz, PC=C), 132.1 (d, ${}^4J_{CP}$ = 3.1 Hz, *p*-PPh), 130.7 (d, ${}^{3}J_{CP}$ = 11.5 Hz, *m*-PPh), 129.8 (s, ArC⁵), 129.0 (d, ${}^{2}J_{CP}$ = 12.4 Hz, o-PPh), 127.4 (d, ${}^{1}J_{CP}$ = 73.5 Hz, ipso-PPh), 125.6 (d, ${}^{3}J_{CP} = 5.0 \text{ Hz}$, ArC⁶), 119.3 (d, ${}^{3}J_{CP} = 5.1 \text{ Hz}$, Ar C^2), 118.6 (d, ${}^{5}J_{CP}$ = 1.1 Hz, Ar C^4), 27.8 (d, ${}^{3}J_{CP}$ = 13.1 Hz, C_a-CH₂-CH₂), 22.6 (s, C_q-CH₂-CH₂) ppm. ³¹P NMR (101.25 MHz, CDCl₃): δ = 54.2 (s) ppm. HRMS (EI): calcd. for C₂₆H₂₁N₆PS [M] 480.1286, found 480.1307; m/z (%) = 480 (100) [M]⁺, 452 (3) [M - N_2]⁺. IR (KBr): $\tilde{v} = 3047$ (w), 2942 (w), 2856 (w), 2108 (s, N_3), 1595 (m), 1575 (m), 1480 (w), 1436 (w), 1419 (w), 1297 (m), 1095 (w), 789 (w), 746 (w), 717 (m), 690 (m), 670 (w) cm^{-1} . UV/Vis (CH₂Cl₂): $\lambda_{abs} = 244$ ($\epsilon = 3.85 \times 10^4 \, \text{M}^{-1} \, \text{cm}^{-1}$), 328 nm ($\epsilon =$ $8.85 \times 10^3 \text{ m}^{-1} \text{ cm}^{-1}$).

Crystal Structure Determination of 8: C₂₆H₂₁N₆PS (480.52), yellow plate, $0.18 \times 0.12 \times 0.06$ mm, monoclinic, $P2_1/c$ (no. 14), a =10.0280(1), b = 15.1083(2), c = 17.6600(2) Å, $\beta = 119.0155(5)^{\circ}$, V = 2339.78(5) Å³, Z = 4, D_X = 1.364 g/cm³, μ = 0.24 mm⁻¹. 39210 reflections were measured with a Nonius Kappa CCD diffractometer with rotating anode and graphite monochromator (λ = 0.71073 Å) up to a resolution of $(\sin \theta / \lambda)_{max} = 0.65 Å^{-1}$ at a temperature of 150(2) K. Intensity data were integrated with the HKL2000 software.^[19] Absorption correction and scaling were performed based on multiple measured reflections with SADABS^[20] (0.77–0.98 correction range). 5358 reflections were unique (R_{int} = 0.057), of which 3995 were observed $[I > 2\sigma(I)]$. The structure was solved with Direct Methods using the program SHELXS-97^[21] and refined with SHELXL-97^[21] against F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps and refined with a riding model. 307 parameters were refined with no restraints. R_1/wR_2 [I>2 σ (I)] = 0.0402/0.0914. R_1/wR_2 (all refl.) = 0.0647/0.1026. S = 1.029. Residual electron density between -0.25 and 0.32 e/Å³. Geometry calculations and checking for higher symmetry were performed with the PLATON program.^[22] CCDC-853315 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

2,5-Bis(4-phenyl-1*H*-1,2,3-triazol-1-yl)-1-phenyl-1-thiooxophosphole (9a): A solution of 8 (48.0 mg, 100 µmol), phenylacetylene (44.0 µL, 400 µmol, 4 equiv.), 2,6-lutidine (23.4 µL, 200 µmol, 2 equiv.) and $[Cu(NCMe)_4][PF_6]$ (1.9 mg, 5.0 $\mu mol,$ 0.05 equiv.) in CH₂Cl₂ (3 mL) was stirred at room temperature for 64 h and subsequently diluted with CH₂Cl₂ and washed with water. The organic layer was dried with MgSO₄, filtered, and the solvents were removed in vacuo. The yellow crude product was purified by column chromatography on silica gel eluting with hexane/EtOAc, 1:1 ($R_{\rm F}$ = 0.38) to obtain **9a** as a yellow powder (67.9 mg, 99.2 μ mol, 99%). M.p. 136.0–136.4 °C. ¹H NMR (400.13 MHz, CDCl₃): δ = 8.07 (s, 2 H, NCH), 7.89 (dd, ${}^{3}J_{HH} = 8.3$, ${}^{4}J_{HH} = 1.3$ Hz, 2 H, *o*-PhH), 7.85 (dd, ${}^{3}J_{\text{HH}} = 8.2$, ${}^{4}J_{\text{HH}} = 1.5$ Hz, 2 H, *o*-PPhH), 7.83 (t, ${}^{4}J_{\text{HH}}$ = 1.1 Hz, 2 H, Ar H^2), 7.70–7.76 (m, 2 H, Ar H^6), 7.51 (tt, ${}^3J_{\rm HH}$ = 7.3, ${}^{4}J_{HH} = 1.5$ Hz, 1 H, *p*-PPh*H*), 7.42–7.49 (m, 10 H, *m*-Ph*H*, *m*-PPhH, Ar $H^{4,5}$), 7.37 (tt, ${}^{3}J_{HH} =$ 7.4, ${}^{4}J_{HH} =$ 1.3 Hz, 2 H, *p*-PhH), 2.90 (dd, ${}^{2}J_{HH}$ = 18.1, ${}^{4}J_{HP}$ = 3.7 Hz, 2 H, C_q-CH₂-CH₂), 2.83 (dd,

 ${}^{2}J_{\text{HH}} = 18.1, {}^{4}J_{\text{HP}} = 3.2 \text{ Hz}, 2 \text{ H}, C_{q}\text{-}CH_{2}\text{-}CH_{2}), 1.83 \text{ (t, } {}^{3}J_{\text{HH}} = 1.00 \text{ Hz}$ 2.7 Hz, 4 H, C_q-CH₂-CH₂) ppm. ¹³C NMR (62.90 MHz, CDCl₃): $\delta = 149.4$ (d, ${}^{2}J_{CP} = 22.0$ Hz, PC=C), 148.4 (s, NCH=C), 136.9 (s, Ar C^3), 134.1 (d, ${}^2J_{CP}$ = 12.6 Hz, Ar C^1), 133.2 (d, ${}^1J_{CP}$ = 81.8, PC=C), 132.2 (d, ${}^{4}J_{CP}$ = 3.2 Hz, *p*-PPh), 130.6 (d, ${}^{2}J_{CP}$ = 11.3 Hz, o-PPh), 130.1 (s, *ipso*-Ph), 129.8 (s, ArC⁴), 129.1 (d, ${}^{3}J_{CP} = 6.3$ Hz, *m*-PPh), 129.0 (s, ArC⁵), 128.8 (s, *m*-Ph), 128.4 (s, *p*-Ph), 127.1 (d, ${}^{1}J_{CP}$ = 73.6 Hz, *ipso*-PPh), 125.8 (s, *o*-Ph), 120.5 (d, ${}^{3}J_{CP}$ = 5.0 Hz, Ar C^2), 119.8 (d, ${}^{3}J_{CP}$ = 1.3 Hz, Ar C^6), 117.4 (s, NCH), 27.8 (d, ${}^{3}J_{CP}$ = 13.2 Hz, C_q -CH₂-CH₂), 22.4 (s, C_q -CH₂-CH₂) ppm. ³¹P NMR (101.25 MHz, CDCl₃): δ = 54.4 (s) ppm. HRMS (FAB): calcd. for $C_{42}H_{34}N_6PS$ [M + H] 685.2303, found 685.2296; m/z (%) = 685 (100) [M + H]⁺, 684 (23) [M]⁺, 542 (29) [M - TrPh + 2 H]⁺. IR (neat): $\tilde{v} = 2976$ (w), 2933 (w), 1576 (m), 1477 (m), 1261 (m), 1227 (w), 1093 (s), 1038 (s), 1019 (s), 881 (w), 797 (s), 761 (s), 718 (m), 690 (s), 668 (m) cm⁻¹. UV/Vis (CH₂Cl₂): $\lambda_{abs} = 248$ ($\epsilon =$ $6.08 \times 10^4 \text{ m}^{-1} \text{ cm}^{-1}$), 326 nm ($\varepsilon = 8.23 \times 10^3 \text{ m}^{-1} \text{ cm}^{-1}$). FS (cyclohexane): $\lambda_{\rm em} = 303 \text{ nm} (\Phi_{\rm F} = 0.0019).$

2,5-Bis[4-(pyridin-2-yl)-1H-1,2,3-triazol-1-yl]-1-phenyl-1-thiooxophosphole (9b): A solution of 8 (70.0 mg, 146 µmol), 2-ethynylpyridine (30.3 µL, 300 µmol, 2 equiv.), 2,6-lutidine (34.9 µL, 300 µmol, 2 equiv.) and [Cu(NCMe)₄][PF₆] (2.7 mg, 7.3 µmol, 0.05 equiv.) in CH₂Cl₂ (7 mL) was stirred at room temperature for 64 h and subsequently diluted with CH₂Cl₂ and washed with water. The organic layer was dried with MgSO₄, filtered, and the solvents were removed. The yellow crude product was purified by column chromatography on silica gel eluting with hexane/EtOAc, 1:2 ($R_{\rm E}$ = 0.18) affording **9b** as a yellow powder (83.9 mg, 122 μ mol, 84%). M.p. 77.1–77.5 °C. ¹H NMR (400.13 MHz, CDCl₃): δ = 8.62 (d, ${}^{3}J_{\text{HH}} = 4.5 \text{ Hz}, 2 \text{ H}, \text{Py}H^{6}$), 8.50 (s, 2 H, NCH), 8.22 (d, ${}^{3}J_{\text{HH}} =$ 7.9 Hz, 2 H, PyH³), 7.84 (ddd, ${}^{3}J_{HP} = 13.9$, ${}^{3}J_{HH} = 6.8$, ${}^{4}J_{HH} =$ 1.5 Hz, 2 H, *o*-PPh*H*), 7.81 (br. s, 2 H, Ar H^2), 7.80 (dt, ${}^{3}J_{HH} = 7.9$, ${}^{4}J_{\rm HH}$ = 1.7 Hz, 2 H, PyH⁴), 7.72 (dd, ${}^{3}J_{\rm HH}$ = 7.9, ${}^{4}J_{\rm HH}$ = 0.9 Hz, 2 H, Ar H^4), 7.53 (dd, ${}^{3}J_{HH} = 7.8$, ${}^{4}J_{HH} = 1.0$ Hz, 2 H, Ar H^6), 7.46 (t, ${}^{3}J_{HH} = 7.9$ Hz, 2 H, Ar H^{5}), 7.40–7.51 (m, 3 H, m-PPhH, p-PPh*H*), 7.26 (t, ${}^{3}J_{HH}$ = 5.9 Hz, 2 H, Py*H*⁵), 2.90 (dd, ${}^{2}J_{HH}$ = 18.1, ${}^{4}J_{\rm HP} = 3.5$ Hz, 2 H, C_q-CH₂-CH₂), 2.82 (dd, ${}^{2}J_{\rm HH} = 18.1$, ${}^{4}J_{\rm HP} =$ 3.1 Hz, 2 H, C_q-CH₂-CH₂), 1.82 (t, ${}^{3}J_{HH}$ = 2.8 Hz, 4 H, C_q-CH₂-CH₂) ppm. ¹³C NMR (100.62 MHz, CDCl₃): δ = 149.9 (s, PyC²), 149.5 (s, PyC⁶), 149.3 (d, ${}^{2}J_{CP}$ = 22.1 Hz, PC=C), 149.0 (s, NCH=*C*), 136.94 (s, Py*C*⁴), 136.94 (s, Ar*C*³), 134.3 (d, ${}^{2}J_{CP}$ = 12.7 Hz, Ar C^1), 133.4 (d, ${}^1J_{\rm CP}$ = 81.2 Hz, PC=C), 132.3 (d, ${}^4J_{\rm CP}$ = 3.0 Hz, *p*-PPh), 130.6 (d, ${}^{2}J_{CP}$ = 11.6 Hz, *o*-PPh), 129.9 (s, ArC⁵), 129.3 (d, ${}^{3}J_{CP}$ = 4.5 Hz, ArC⁶), 129.1 (d, ${}^{3}J_{CP}$ = 12.5 Hz, *m*-PPh), 127.0 (d, ${}^{1}J_{CP}$ = 74.1 Hz, *ipso*-PPh), 123.1 (s, PyC⁵), 120.6 (d, ${}^{3}J_{CP}$ = 5.6 Hz, ArC²), 120.4 (s, PyC³), 119.8 (s, NCH), 119.8 (d, ${}^{3}J_{CP}$ = 1.1 Hz, ArC⁴), 27.9 (d, ${}^{3}J_{CP}$ = 12.8 Hz, C_q-CH₂-CH₂), 22.5 (s, C_q-CH₂-*C*H₂) ppm. ³¹P NMR (101.25 MHz, CDCl₃): δ = 54.3 (s) ppm. HRMS (FAB): calcd. for $C_{42}H_{32}N_8PS$ [M + H] 687.2208, found $687.2214; m/z (\%) = 687 (100) [M + H]^+, 686 (16) [M]^+. IR (neat):$ $\tilde{v} = 2920$ (w), 2853 (w), 1718 (w), 1600 (w), 1584 (w), 1472 (w), 1437 (w), 1414 (w), 1260 (m), 1150 (m), 1065 (m), 1023 (s), 784 (s), 748 (w), 692 (m) cm⁻¹. UV/Vis (CH₂Cl₂): $\lambda_{abs} = 245$ ($\varepsilon =$ $4.66 \times 10^4 \text{ m}^{-1} \text{ cm}^{-1}$), 286 ($\varepsilon = 3.06 \times 10^4 \text{ m}^{-1} \text{ cm}^{-1}$), 324 nm ($\varepsilon =$ $7.52 \times 10^3 \text{ m}^{-1} \text{ cm}^{-1}$). FS (cyclohexane): $\lambda_{\text{em}} = 302 \text{ nm} (\Phi_{\text{F}} =$ 0.0036).

2,5-Bis[4-(thien-2-yl)-1*H***-1,2,3-triazol-1-yl]-1-phenyl-1-thiooxophosphole (9c):** A solution of **8** (21.5 mg, 44.7 μ mol), 2-ethynylthiophene (0.15*M* in CH₂Cl₂, 1.0 mL, 150 μ mol, 3.35 equiv.), 2,6-lutidine (10.4 μ L, 89.5 μ mol, 2 equiv.) and [Cu(NCMe)₄][PF₆] (0.83 mg, 2.2 μ mol, 0.05 equiv.) in CH₂Cl₂ (4 mL) was stirred at room temperature for 64 h and subsequently diluted with CH₂Cl₂ and washed with water. The organic layer was dried with MgSO₄,

filtered, and the solvents were removed. The yellow crude product was purified by column chromatography on silica gel eluting with hexane/EtOAc, 2:1 ($R_{\rm F} = 0.15$) to obtain 9c as a yellow powder (25.5 mg, 36.6 μmol, 82%). M.p. 150.5–151.0 °C. ¹H NMR (400.13 MHz, CDCl₃): δ = 7.97 (s, 2 H, NCH), 7.89 (ddd, ³J_{HP} = 13.9, ${}^{3}J_{\text{HH}} = 7.7$, ${}^{4}J_{\text{HH}} = 1.4$ Hz, 2 H, *o*-PPh*H*), 7.79 (t, ${}^{4}J_{\text{HH}} =$ 1.0 Hz, 2 H, Ar H^2), 7.75 (dt, ${}^{3}J_{HH} = 6.6$, ${}^{4}J_{HH} = 1.0$ Hz, 2 H, Ar H^6), 7.53–7.57 (m, ${}^{3}J_{HH} = 7.2$, ${}^{4}J_{HH} = 1.6$ Hz, 1 H, *p*-PPhH), 7.46–7.52 (m, 8 H, thienyl H^5 , m-PPhH, Ar $H^{4,5}$), 7.37 (dd, ${}^{3}J_{\rm HH}$ = 5.1, ${}^{3}J_{HH} = 1.1 \text{ Hz}$, 2 H, thienyl H^{3}), 7.14 (dd, ${}^{3}J_{HH} = 5.1$, ${}^{3}J_{HH} =$ 3.6 Hz, 2 H, thienyl H^4), 2.92 (dd, ${}^2J_{HH}$ = 18.2, ${}^4J_{HP}$ = 3.7 Hz, 2 H, C_q - CH_2 - CH_2), 2.84 (dd, ${}^2J_{HH}$ = 18.2, ${}^4J_{HP}$ = 3.2 Hz, 2 H, C_q - CH_2 -CH₂), 1.86 (t, ${}^{3}J_{HH}$ = 2.9 Hz, 4 H, C_q-CH₂-CH₂) ppm. ${}^{13}C$ NMR $(100.62 \text{ MHz}, \text{CDCl}_3): \delta = 149.4 \text{ (d}, {}^2J_{\text{CP}} = 22.2 \text{ Hz}, \text{PC}=C), 143.41$ (s, NCH=*C*), 136.7 (s, Ar*C*³), 134.1 (d, ${}^{2}J_{CP}$ = 12.5 Hz, Ar*C*¹), 133.1 (d, ${}^{1}J_{CP}$ = 81.1 Hz, PC=C), 132.3 (d, ${}^{4}J_{CP}$ = 3.3 Hz, p-PPh), 132.2 (s, thienyl C^2), 130.6 (d, ${}^2J_{CP}$ = 11.6 Hz, *o*-PPh), 129.8 (s, ArC⁴), 129.1 (s, ArC⁵), 129.0 (d, ${}^{3}J_{CP}$ = 8.3 Hz, *m*-PPh), 127.6 (s, thienyl C^5), 127.0 (d, ${}^{1}J_{CP}$ = 73.9 Hz, *ipso*-PPh), 125.3 (s, thienyl C^4), 124.5 (s, thienyl C^3), 120.4 (d, ${}^{3}J_{CP}$ = 5.2 Hz, Ar C^2), 119.8 (s, Ar C^6), 116.8 (s, NCH), 27.8 (d, ${}^{3}J_{CP}$ = 12.9 Hz, C_q-CH₂-CH₂), 22.4 (s, C_q-CH₂-CH₂) ppm. ³¹P NMR (101.25 MHz, CDCl₃): δ = 54.4 (s) ppm. HRMS (FAB): calcd. for C₃₈H₃₀N₆PS₃ [M + H] 697.1432, found 697.1443; m/z (%) = 697.14 (100) [M + H]⁺, 696.15 (10) [M]⁺. IR (neat): $\tilde{v} = 2993$ (w), 2863 (w), 1576 (m), 1477 (m), 1260 (m), 1233 (m), 1093 (m), 1039 (s), 1016 (s), 999 (w), 965 (w), 930 (w), 892 (w), 857 (w), 787 (s), 747 (w), 716 (m), 689 (s), 670 (s) cm⁻¹. UV/ Vis (CH₂Cl₂): $\lambda = 227$ ($\varepsilon = 2.16 \times 10^4 \text{ m}^{-1} \text{ cm}^{-1}$), 275 ($\varepsilon =$ $1.96 \times 10^4 \text{ m}^{-1} \text{ cm}^{-1}$), 339 nm ($\varepsilon = 3.58 \times 10^3 \text{ m}^{-1} \text{ cm}^{-1}$). FS (cyclohexane): $\lambda_{\rm em} = 302 \text{ nm} (\Phi_{\rm F} = 0.00071).$

2,5-Bis(4-phenyl-1*H*-1,2,3-triazol-1-yl)-1-phenylphosphole (10a): Compound 9a (32.6 mg, 47.6 µmol) was dissolved in toluene (5 mL), and a 1.5 M solution of $P(NMe_2)_3$ in THF (160 μ L, 238 µmol, 5 equiv.) was added. The yellow reaction mixture was refluxed for 16 h, after which the solvent was removed, and the vellow residue was purified by column chromatography on silica gel eluting with hexane/EtOAc, 3:1 ($R_{\rm F} = 0.28$) to obtain 10a a yellow powder (25.9 mg, 39.6 µmol, 83%). ¹H NMR (400.13 MHz, CDCl₃): δ = 8.12 (s, 2 H, NCH), 7.91 (dd, ${}^{3}J_{HH}$ = 8.3, ${}^{4}J_{HH}$ = 1.3 Hz, 4 H, o-PhH), 7.79 (s, 2 H, ArH²), 7.61 (dd, ${}^{3}J_{HH} = 7.0$, ${}^{4}J_{\rm HH}$ = 2.2 Hz, 2 H, Ar H^{4}), 7.45–7.56 (m, 8 H, Ar $H^{5,6}$, *m*-PhH), 7.38 (tt, ${}^{3}J_{HH} = 7.3$, ${}^{4}J_{HH} = 1.3$ Hz, 2 H, *p*-PhH), 7.22–7.29 (m, 2 H, *o*-PPh*H*), 7.21 (t, ${}^{3}J_{HH}$ = 7.2 Hz, 1 H, *p*-PPh*H*), 7.16 (t, ${}^{3}J_{HH}$ = 7.2 Hz, 2 H, m-PPhH), 2.74–3.04 (m, 4 H, C_q-CH₂-CH₂), 1.68– 1.90 (m, 4 H, C_q-CH₂-CH₂) ppm. ¹³C NMR (62.90 MHz, CDCl₃): $\delta = 148.3$ (s, NCH=C), 145.7 (d, ${}^{2}J_{CP} = 10.8$ Hz, PC=C), 142.7 (d, ${}^{1}J_{CP}$ = 2.1 Hz, PC=C), 138.8 (d, ${}^{2}J_{CP}$ = 18.6 Hz, ArC¹), 137.0 (s, Ar C^3), 133.5 (d, ${}^2J_{CP}$ = 18.9 Hz, o-PPh), 130.2 (s, *ipso-Ph*), 129.6 (s, Ar C^5), 129.5 (d, ${}^4J_{CP}$ = 1.4 Hz, *p*-PPh), 129.2 (d, ${}^3J_{CP}$ = 9.4 Hz, ArC⁶), 128.8 (s, *m*-Ph), 128.6 (d, ${}^{3}J_{CP}$ = 8.3 Hz, *m*-PPh), 128.3 (s, *p*-Ph), 125.8 (s, *o*-Ph), 120.6 (d, ${}^{3}J_{CP} = 9.1$ Hz, ArC²), 118.2 (s, ArC⁴), 117.4 (s, NCH), 27.9 (d, ${}^{3}J_{CP}$ = 0.9 Hz, C_q-CH₂-CH₂), 23.0 (s, C_q-CH₂-CH₂) ppm; *ipso*-PPh was unresolved. ³¹P NMR (101.25 MHz, CDCl₃): δ = 13.6 (s) ppm. HRMS (FAB): calcd. for $C_{42}H_{34}N_6P [M + H] 653.2583$, found 653.2592; m/z (%) = 653 (100) $[M + H]^+$, 652 (22) $[M]^+$. UV/Vis (CH₂Cl₂): $\lambda_{abs} = 243$ ($\varepsilon =$ $8.58 \times 10^4 \text{ m}^{-1} \text{ cm}^{-1}$), 290 ($\varepsilon = 2.63 \times 10^4 \text{ m}^{-1} \text{ cm}^{-1}$), 355 nm ($\varepsilon =$ $1.62 \times 10^4 \text{ m}^{-1} \text{ cm}^{-1}$). FS (cyclohexane): $\lambda_{\text{em}} = 463 \text{ nm} (\Phi_{\text{F}} = 0.273)$.

2,5-Bis[4-(pyridin-2-yl)-1*H***-1,2,3-triazol-1-yl]-1-phenylphosphole (10b):** Compound **9b** (83.9 mg, 122 μ mol) was dissolved in toluene (10 mL), and a 1.5 M solution of P(NMe₂)₃ in THF (400 μ L, 600 μ mol, 5 equiv.) was added. The yellow reaction mixture was refluxed for 16 h, after which the solvent was removed, and the

yellow residue was purified by column chromatography on silica gel eluting hexane/EtOAc, 1:2 ($R_{\rm F} = 0.25$), which afforded 10b as a vellow powder (80.0 mg, 122 µmol, 100%). ¹H NMR (400.13 MHz, CDCl₃): $\delta = 8.61 - 8.68$ (m, 2 H, PyH⁶), 8.64 (s, 2 H, NCH), 8.29 (t, ${}^{4}J_{HH} = 7.4 \text{ Hz}, 2 \text{ H}, \text{Py}H^{4}$), 7.88 (s, 2 H, Ar H^{2}), 7.84 (dd, ${}^{3}J_{HH}$ = 7.8, ${}^{4}J_{\text{HH}}$ = 1.9 Hz, 2 H, Py H^{5}), 7.64–7.70 (m, 2 H, Ar H^{4}), 7.47– 7.57 (m, 4 H, ArH^{5,6}), 7.24–7.34 (m, 3 H, o-PPhH, p-PPhH), 7.20 $(dt, {}^{3}J_{HH} = 5.9, {}^{4}J_{HH} = 1.4 \text{ Hz}, 2 \text{ H}, m\text{-PPh}H), 2.71-3.14 (m, 4 \text{ H}, 4 \text{ H})$ Cq-CH2-CH2), 1.68–1.97 (m, 4 H, Cq-CH2-CH2) ppm. ¹³C NMR $(62.90 \text{ MHz}, \text{CDCl}_3): \delta = 149.9 \text{ (s, Py}C^2), 149.3 \text{ (s, Py}C^6), 148.7 \text{ (s,}$ NCH=C), 145.6 (d, ${}^{2}J_{CP}$ = 10.9 Hz, PC=C), 143.0 (d, ${}^{1}J_{CP}$ = 2.1 Hz, *PC*=C), 138.8 (d, ${}^{2}J_{CP}$ = 18.8 Hz, Ar*C*¹), 137.0 (s, Py*C*⁴), 136.9 (s, ArC³), 133.4 (d, ${}^{2}J_{CP}$ = 18.9 Hz, *o*-PPh), 130.8 (d, ${}^{2}J_{CP}$ = 71.4 Hz, ipso-PPh), 130.1 (s, p-PPh), 129.7 (s, ArC⁵), 129.4 (d, ³J_{CP} = 10.2 Hz, ArC⁶), 128.6 (d, ${}^{3}J_{CP}$ = 8.3 Hz, *m*-PPh), 123.0 (s, PyC⁵), 120.4 (s, PyC³), 120.4 (d, ${}^{3}J_{CP}$ = Hz, ArC²), 119.6 (s, ArC⁴), 118.1 (s, NCH), 27.9 (d, ${}^{3}J_{CP} = 0.9$ Hz, C_q-CH₂-CH₂), 23.0 (s, C_q-CH₂-*C*H₂) ppm. ³¹P NMR (101.25 MHz, CDCl₃): δ = 13.5 (s) ppm. HRMS (FAB): calcd. for C₄₀H₃₁N₈P [M] 655.2488, found $655.2473; m/z (\%) = 655 (75) [M + H]^+, 654 (30) [M]^+, 615 (100)$ $[M - C_2H_2N]^+$. UV/Vis (CH₂Cl₂): $\lambda_{abs} = 238$ ($\varepsilon =$ $5.29 \times 10^4 \text{ m}^{-1} \text{ cm}^{-1}$), 286 ($\varepsilon = 2.81 \times 10^4 \text{ m}^{-1} \text{ cm}^{-1}$), 355 nm ($\varepsilon =$ $1.13 \times 10^4 \text{ m}^{-1} \text{ cm}^{-1}$). FS (cyclohexane): $\lambda_{\text{em}} = 469 \text{ nm} (\Phi_{\text{F}} = 0.134)$.

2,5-Bis[4-(thien-2-yl)-1H-1,2,3-triazol-1-yl]-1-phenylphosphole (10c): Compound 9c (13.4 mg, 19.2 µmol) was dissolved in toluene (3.5 mL) and a 1.5 M solution of $P(NMe_2)_3$ in THF (70 μ L, 100 µmol, 5 equiv.) was added. The yellow reaction mixture was refluxed for 16 h, after which the solvent was removed, and the yellow residue was purified by column chromatography on silica gel eluting with hexane/EtOAc, 2:1 to 1:1 [$R_{\rm F}$ (1:1) = 0.56] to obtain 10c as a yellow powder (9.0 mg, 13.5 μ mol, 71%). ¹H NMR (400.13 MHz, CDCl₃): δ = 8.03 (s, 2 H, NCH), 7.71 (br. s, 2 H, Ar H^2), 7.62 (dd, ${}^{3}J_{HH} = 8.8$, ${}^{4}J_{HH} = 2.4$ Hz, 2 H, Ar H^4), 7.47–7.51 (m, 6 H, Ar $H^{5,6}$, thienyl H^2), 7.36 (d, ${}^{3}J_{HH} = 5.0$ Hz, 2 H, thienyl H^3), 7.26–7.29 (m, 2 H, *o*-PPhH), 7.24 (t, ${}^{3}J_{HH}$ = 7.2 Hz, 1 H, *p*-PPh*H*), 7.19 (t, ${}^{3}J_{HH} = 7.2$ Hz, 2 H, *m*-PPh*H*), 7.14 (dd, ${}^{3}J_{HH} =$ 5.0, ${}^{3}J_{HH} = 3.8 \text{ Hz}$, 2 H, thienyl H^{4}), 2.98–3.08 (m, 2 H, C_q-CH₂-CH₂), 2.76–2.84 (m, 2 H, C_q-CH₂-CH₂), 1.86–1.92 (m, 2 H, C_q-CH₂-CH₂), 1.76–1.82 (m, 2 H, C_q-CH₂-CH₂) ppm. ¹³C NMR (62.90 MHz, CDCl₃): δ = 145.7 (d, ²J_{CP} = 11.0 Hz, PC=C), 143.4 (s, thienylC²), 142.7 (d, ${}^{1}J_{CP}$ = 1.9 Hz, PC=C), 138.8 (d, ${}^{2}J_{CP}$ = 18.7 Hz, ArC^{1}), 136.8 (s, ArC^{3}), 133.5 (d, ${}^{2}J_{CP}$ = 19.0 Hz, o-PPh), 132.4 (s, NCH=*C*), 131.8 (d, ${}^{4}J_{CP}$ = 2.8 Hz, *p*-PPh), 130.5 (d, ${}^{1}J_{CP}$ = 12.0 Hz, *ipso*-PPh), 129.6 (s, ArC⁵), 129.3 (d, ${}^{3}J_{CP}$ = 9.4 Hz, ArC⁶), 128.6 (d, ${}^{3}J_{CP}$ = 8.3 Hz, *m*-PPh), 127.6 (s, thienylC⁵), 125.3 (s, thienyl C^4), 124.5 (s, thienyl C^3), 120.5 (d, ${}^{3}J_{CP} = 8.9$ Hz, Ar C^2), 118.2 (s, ArC⁴), 116.9 (s, NCH), 27.9 (d, ${}^{3}J_{CP} = 1.4 \text{ Hz}, C_{q}-CH_{2}-$ CH₂), 23.0 (s, C_q-CH₂-CH₂) ppm. ³¹P NMR (101.25 MHz, CDCl₃): δ = 13.8 (s) ppm. HRMS (FAB): calcd. for C₃₈H₃₀N₆PS₂ [M + H] 665.1711, found 665.1718; m/z (%) = 665 (100) [M +H]⁺, 664 (31) [M]⁺. UV/Vis (CH₂Cl₂): $\lambda_{abs} = 276$ ($\varepsilon =$ $3.23 \times 10^4 \text{ m}^{-1} \text{ cm}^{-1}$), 356 nm ($\varepsilon = 1.02 \times 10^4 \text{ m}^{-1} \text{ cm}^{-1}$). FS (cyclohexane): $\lambda_{em} = 460 \text{ nm} (\Phi_{F} = 0.309).$

Computational Details: All theoretical calculations were performed using the Amsterdam Density Functional (ADF) program suite.^[23] Geometries were optimized using the TZ2P basis set. The inner cores of the carbon, nitrogen, and oxygen atoms (1s²) and those of the sulfur and phosphorus atoms (1s²2s²2p⁶) were kept frozen. An auxiliary set of STOs was used to fit the density for the Coulombtype integrals. The GGA exchange functional OPTX was used in combination with the non-empirical PBE correlation functional (OPBE) with an integration accuracy of 5.0 and convergence criteria of 1×10^{-5} . Coordinates of the optimized structures can be found in the Supporting Information. All TDDFT calculations were performed using the quantum chemical package of programs Gaussian 09.^[24] The geometries were optimized at the OPBE/cc-pVTZ level. Solvent effects of tetrahydrofuran (THF) were taken into account with the Polarizable Continuum Model (PCM). The vertical excitation energies and oscillator strengths have been calculated by TDDFT in combination with a linear response of solvation (PCM-LR) at the CAM-B3LYP/cc-pVTZ level.^[25]

Supporting Information (see footnote on the first page of this article): Lifetimes, quantum yields and decay constants for 9b and 10ac, the CV of 9a at low temperature, all NMR spectra, and the computed coordinates of the optimized structures of 9a-c and 10a-c.

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