

Phosphorus Heterocycles

Phosphorus Post-Functionalization of Diphosphahexaarenes

Philip Hindenberg,^[a] Frank Rominger,^[a] and Carlos Romero-Nieto^{*[a, b]}

Abstract: Diphosphahexaarenes are highly stable π -extended frameworks containing two six-membered phosphorus heterocycles that have emerged recently. Herein, we present a detailed investigation on the post-functionalization reactions of their phosphorus centers with special emphasis on the selectivity of the processes and the impact of the phosphorus functionalizations into the physicochemical proper-

ties. These studies reveal that indeed the phosphorus atoms of the diphosphahexaarenes are readily available to be functionalized with quaternizing and oxidizing agents as well as borane groups without compromising the stability of the system. In addition, the optoelectronic properties of the diphosphahexaarenes are impacted by the phosphorus post-modifications.

Introduction

π -Extended arenes have attracted the attention of materials scientists in the last few decades owing to their beneficial characteristics such as good charge mobilities and often outstanding optical properties.^[1–3] These physicochemical properties have found applications in sensors, field-effect transistors, and light-emitting diodes.^[1–6] In particular, the efficient electronic delocalization within the π -systems is responsible for the optoelectronic properties of arenes. However, large arenes generally come hand in hand with solubility and stability problems, limiting the investigation of their optoelectronic properties. In particular, linearly fused systems with more than five benzene units are prone to oxidation and dimerization.^[2,3,7–11] Importantly, the introduction of six-membered phosphorus heterocycles into the framework of π -extended systems often leads to lowering both the LUMO and HOMO and thus decreases the chance of oxidative or photodecomposition.^[12] In 2018, our group reported the synthesis and optoelectronic properties of novel diphosphahexaarenes.^[13] Indeed, the introduction of two six-membered phosphorus heterocycles into large linearly fused arenes, in combination with two off-linear

benzene rings, led to an outstanding stability and remarkable solubility in common organic solvents.^[13]

In the context of materials science, ideal would be to conceive new arene derivatives whose characteristics could be easily tailored to specific applications by means of facile post-functionalization reactions. This would allow reduced synthetic costs; a defined framework would serve for diverse applications after simple post-modification, avoiding the need to develop synthetic alternatives. To that end, phosphorus heterocycles are particularly attractive owing to their unique post-synthetic possibilities at the phosphorus atom.^[12,14–16] Typical reactions involve the oxidation/reduction of the phosphorus centers as well as coordination of the trivalent state. As an important requirement to fulfill, however, the post-modified arenes should preserve their stability and solubility to allow the processing of the materials. Thus, we targeted the investigation of the phosphorus functionalization of diphosphahexaarenes and the impact of the latter in their physicochemical properties. Reported studies about the post-functionalizations of systems based on six-membered phosphorus heterocycles have, to date, mostly involved small fused compounds;^[12,15,17] it is therefore unclear whether the latter methodologies may be applied to larger π -extended systems. Side reactions or decomposition of the materials due to the largely extended molecular frontier orbitals are potential handicaps in our approach.

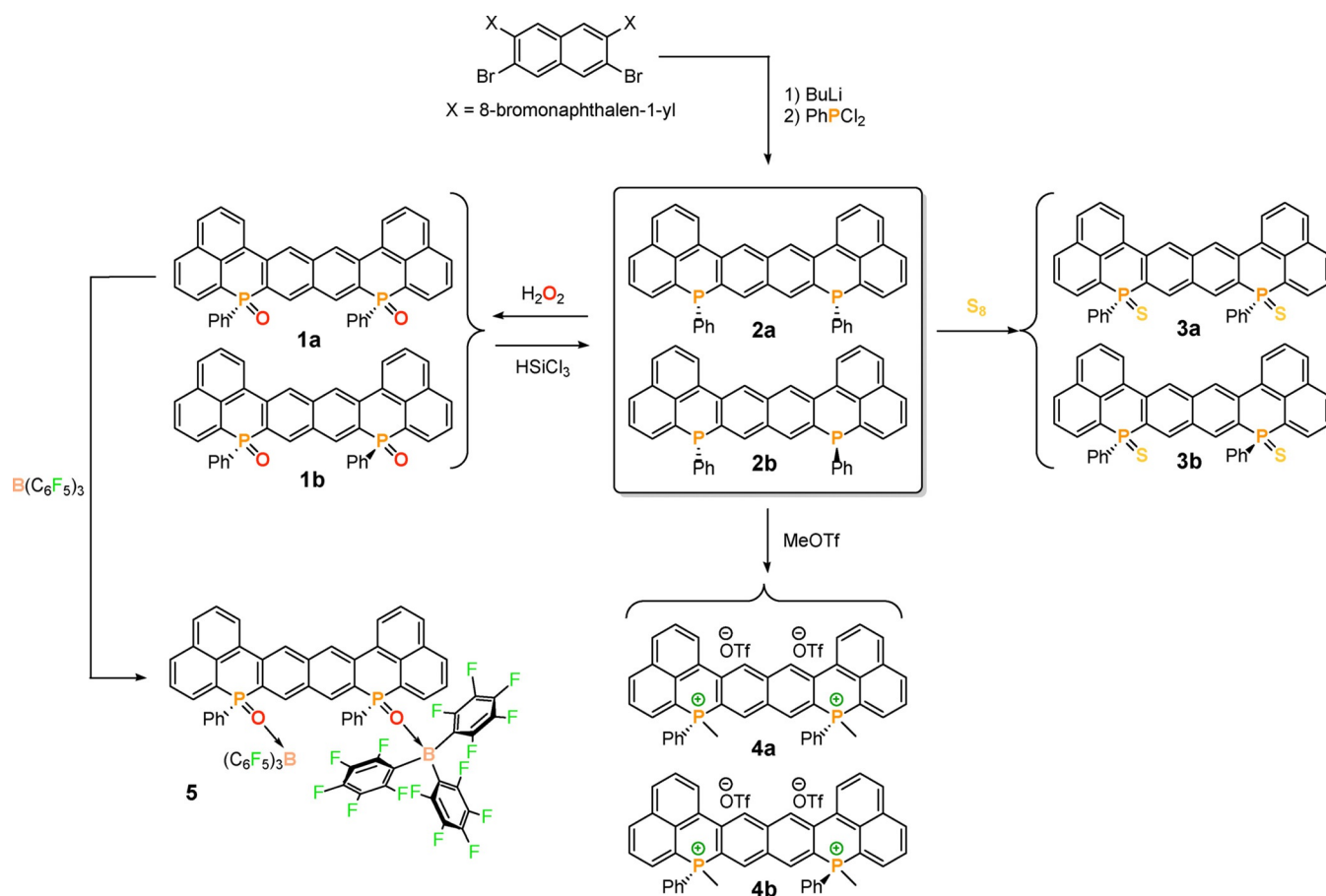
Results and Discussion

For our investigations, we chose the *cis*-derivative **1a** (Scheme 1) owing to a) its straightforward preparation,^[13] b) the significant contribution of the phosphorus atom into the LUMO orbital, and c) its 84% fluorescence quantum yield. As reported previously,^[13] the isolation of the *cis*-derivative **1a** involve its separation from the corresponding *trans*-isomer **1b** by column chromatography. First, we investigated the reduction of the phosphorus centers of **1a** from λ^5 ; σ^2 -endo, σ^2 -

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Scheme 1. Synthesis of diphosphahexaarenes 1–5.

exo^[12a] to λ^3 ; σ^2 -*endo*, σ^1 -*exo*. It is important to highlight that within heterocyclic systems, the phosphorus atoms hardly invert due to their relatively high inversion barrier.^[18–20] However, several reduction conditions tested with the *cis*-derivative **1a** led to the mixture of isomers containing **2a** and **2b** (Scheme 1). In particular, the treatment of **1a** with borane dimethylsulfide followed by triethylamine, a method that has been shown to take place under retention of the phosphorus configuration in bicyclic phosphine oxides,^[21–23] led to the isomer mixture **2a** and **2b**. By the same token, the reduction with an excess of trichlorosilane was reported for tertiary phosphine oxides to take place with retention of the configuration.^[24,25] However, the reaction of **1a** with an increasing amount of trichlorosilane (see the Supporting Information for details) provided again both isomers of **2a** and **2b**. It is worth remarking that the reduction of the phosphorus centers required longer reaction times and relatively more equivalents of trichlorosilane than for the phosphaphenylene derivatives.^[15] The addition of sacrificial triethyl phosphite as a method to accelerate the reduction^[26] was unsuccessful. It should be noted that the reduced compounds **2a** and **2b** easily re-oxidized under air atmosphere, which ultimately hampered their separation.

With **2a,b** in hand, we investigated the feasibility to oxidize the phosphorus centers with sulfur. Thus, the addition of elemental sulfur^[116b,d,27,28] led to the quantitative conversion of

2a,b into **3a,b**. Like **1a,b**,^[13] **3a,b** were highly stable towards light and air. However, in stark contrast to derivatives **1**, the isomers of **3** showed a relatively more limited solubility in common organic solvents. Nevertheless, we could separate them by standard column chromatography.

On the other hand, we explored the possibility to quaternize the phosphorus centers of **2a** and **2b** and obtain the corresponding dicationic derivatives **4a,b** (Scheme 1). Indeed, the reaction of **2** with methyl triflate at 0 °C yielded the charged derivatives **4a,b**, now featuring λ^4 ; σ^2 -*endo* σ^2 -*exo* configuration.^[12a] Compounds **4** were stable and soluble in polar solvents such as ethyl acetate, acetone, acetonitrile, ethanol, methanol, and even partially soluble in water. The tetrahedral λ^4 ; σ^2 -*endo* σ^2 -*exo* phosphorus atoms appear thus to effectively prevent strong π -stacking in extended arenes.

Finally, in addition to the standard phosphorus post-functionalizations, we investigated the possibility to additionally post-functionalize the oxidized λ^5 ; σ^2 -*endo*, σ^2 -*exo* phosphorus centers by coordination of Lewis acid B(C₆F₅)₃ (BCF) as a means to further modify the features of the diphosphahexaarenes.

The addition of two equivalents of BCF to **1a** at room temperature quantitatively led to derivative **5**, which was rather sensitive to hydrolysis. However, no decomposition was observed under repeated cycles of heating at 150 °C. To corroborate the formation of the borane adduct, we obtained its struc-

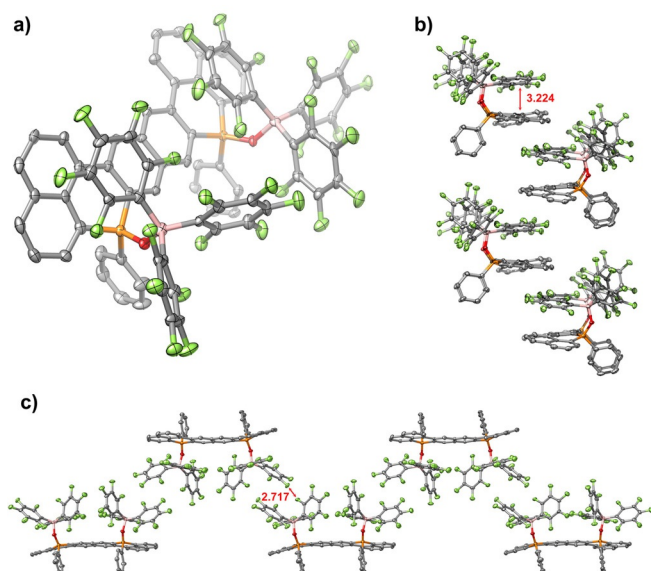


Figure 1. X-ray structure of **5**. Molecular structure (left) and 3D packing (right and bottom). Ellipsoids drawn at the 50% level of probability. Hydrogen atoms and solvent molecules have been omitted for clarity. Distances are given in angstroms.

ture by single-crystal X-ray diffraction analysis (Figure 1). The latter structure confirmed thus that the coordination did not affect the configuration of the phosphorus centers. Interestingly, a pentafluorophenyl ring of each BCF moiety bends over the positively charged six-membered phosphorus heterocycle with shorter distances in the range of π -stacking: that is, 3.224 Å (Figure 1b). Regarding the 3D distribution, the molecules arrange along one axis by intermolecular interactions between the pentafluorophenyl rings (Figure 1c). The closer distances are F–F interactions; i.e. 2.717 Å. Perpendicular to the latter axis, the molecules organize by π -stacking alternating pentafluorophenyl rings and diphosphahexaarene cores (Figure 1b).

Changes in the phosphorus electronic density after post-functionalization must be reflected in the spectroscopic properties. To investigate the latter, we comparatively analyzed the ^{31}P NMR spectra of all derivatives (see Table S1 in the Supporting Information). Thus, we found the signals of **2a,b** clearly shifted upfield from the ones of the parent oxides **1a,b** by approximately 44 ppm; i.e. to $\delta = -34.63$ and $\delta = -35.43$ ppm for **2a,b** from $\delta = +8.30$ for **1a** and $\delta = +9.06$ ppm for **1b**. The signals of the thio-derivatives **3a,b** were oppositely downfield shifted to $\delta = +21.62$ and $\delta = +21.54$ ppm, respectively, which differ by approximately 13 ppm from the signals of the oxides **1**. It is noteworthy that the upfield shift (the lower shift value) of the oxide relative to the thiooxide can be attributed to a higher d orbital density of phosphorus in P=O and the associated stronger paramagnetic contribution to the chemical shift.^[29,30] In turn, the ^{31}P NMR signals of the two quaternized λ^4 ; σ^2 -endo, σ^2 -exo isomers **4a,b** were shifted to $\delta = -0.57$ and $\delta = -0.61$ ppm, respectively. The approximately 35 ppm downfield shift relative to the trivalent species **2a,b** can be ex-

plained by the electron deficiency of the cationic phosphorus center. Finally, upon coordination of BCF to the oxide **1a**, the ^{31}P NMR signal of **5** was downfield shifted from +8.30 for **1a** to $\delta = +22.17$ ppm due to the electron-withdrawing capacity of the borane group.

To shed light on the electronic properties distribution of the diphosphahexaarene derivatives, we estimated the frontier molecular orbitals by DFT calculations at the B3LYP/6-31+G(d) level of theory. The energy levels are represented in Figure 2 and the electronic density distribution in Figures S1–S3 (in the Supporting Information).

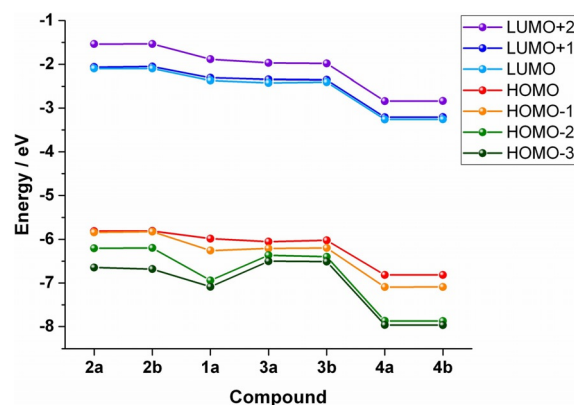


Figure 2. Distribution of the energy levels of compounds **1** to **4** obtained by DFT calculations. See Table S3 in the Supporting Information for values.

Overall, the frontier molecular orbitals appear fully delocalized for compounds **1–4**. It is worth highlighting that although in the phosphorus-functionalized molecules **1**, **3**, and **4**, the LUMO has a significant contribution from the phosphorus atom, the LUMO of the reduced λ^3 ; σ^2 -endo, σ^1 -exo isomers **2a,b** do not include the heteroatom. As an exception, moreover, the LUMO of the quaternized compound **4** is mainly located at the center of the diphosphahexaarene core (Figure S3 in the Supporting Information), whereas the HOMO remains delocalized over the whole system. This points to a feasible intramolecular charge transfer nature for the HOMO/LUMO transition.

In agreement with the observation reported previously for **1**,^[13] DFT calculations predict no significant differences between the energies of the *cis* and *trans* isomers of **2**, **3**, and **4** (Figure 2). On the other hand, the energy of the molecular orbitals is indeed impacted by the post-functionalization of the phosphorus atom.

The trivalent λ^3 ; σ^2 -endo, σ^1 -exo isomer **2** possesses the highest optical band gap, that is, 3.71 eV; both the HOMO/HOMO–1 and LUMO/LUMO+1 appear degenerate. The LUMO/LUMO+1 degeneration persists along the complete series **1** to **4** (Figure 2). The oxidation of the phosphorus centers with H_2O_2 to yield the λ^5 ; σ^2 -endo, σ^2 -exo derivative **1** decreases the optical band gap to 3.61 eV and disrupts the degeneration of the HOMO/HOMO–1. In turn, the transformation of **2** into the sulfur-containing λ^5 ; σ^2 -endo, σ^2 -exo phosphorus derivative **3** does not provide any significant change in the op-

tical band gap compared with **1**; bigger changes are found in the internal molecular orbitals HOMO–1 to HOMO–3, which appear now closer in energy (Table S3 in the Supporting Information). The latter orbitals mostly involve the P=S fragment (Figure S2 in the Supporting Information). Finally, the quaternization of the phosphorus atoms leads to a significant reduction of the energy of all molecular orbitals compared with the trivalent compound **2**; the optical band gap decreases in turn from 3.71 to 3.56 eV for **4**.

To further explore the differences in the energy of molecular orbitals, we subjected the diphosphahexaarene derivatives to electrochemical experiments, that is, cyclic voltammetry, differential pulse voltammetry, and square-wave voltammetry (Figure S5 and Table S4 in the Supporting Information). Thus, the trivalent derivative **2** presents an irreversible oxidation at +1.01 V and two reductions at –1.63 and –1.87 V, which are in sharp contrast to the values found for **1**, +1.77 V, –1.43, and –1.71 V.^[13] The low oxidation potential of **2** is in agreement with its susceptibility to oxidize in air. On the other hand, the pentavalent sulfur derivative **3** exhibits an oxidation at +1.35 V and a reduction wave at –1.44, both irreversible. Finally, **4** presents the lowest reduction potentials with processes at –1.1, –1.26, and –1.6 V; no oxidation was observed under our experimental conditions (see the Supporting Information).

The differences in the electrochemical properties of compounds **1–4** should be reflected in their optical properties. Thus, we turned to steady-state spectroscopic investigations (Table S5 in the Supporting Information, Figure 3). First, it is important to highlight that, as reported for **1**,^[13] we did not observe any photodecomposition of derivatives **2–5** upon repeated cycles of illumination over months.

The reduction of the phosphorus centers of **1** to yield the trivalent species **2** fades out the lower-energy photoinduced transitions. Thus, in CH₂Cl₂ solutions, whereas the oxide **1** possesses absorption maxima at 343, 385, and 405 nm,^[13,31] the trivalent species **2** exhibits a unique absorption band with a maximum at 354 nm and a shoulder at 369 nm. Both isolated thio-derivatives **3 a,b** present absorption maxima at 347 and 405 nm and, in agreement with the theoretical calculations, resemble the absorption features of oxides **1 a,b**.

The absorption spectrum of the quaternized derivatives **4** maximizes at 354, 392, and 414 nm: i.e. the maxima of the quaternized species are bathochromically shifted compared with the oxide, reduced, and thio-derivatives. In view of the water solubility of **4**, we recorded its absorption properties in aqueous solutions (Figure S6 in the Supporting Information), which remained essentially unaltered; i.e. the absorption spectrum maximizes at 348, 392, and 412 nm.

Finally, the most redshifted absorption features were obtained from the borane adduct **5**; the absorption spectrum maximizes at 348, 355, 402, and 424 nm.

The outstanding stability of all diphosphahexaarene derivatives allowed us to investigate the emission properties of all materials (Figure 3b). The diphosphahexaarenes showed uncommon spectroscopic features. Surprisingly, the emission maxima of compounds **1**, **2**, and **3** in CH₂Cl₂ were rather similar, independently from their phosphorus functionalizations;

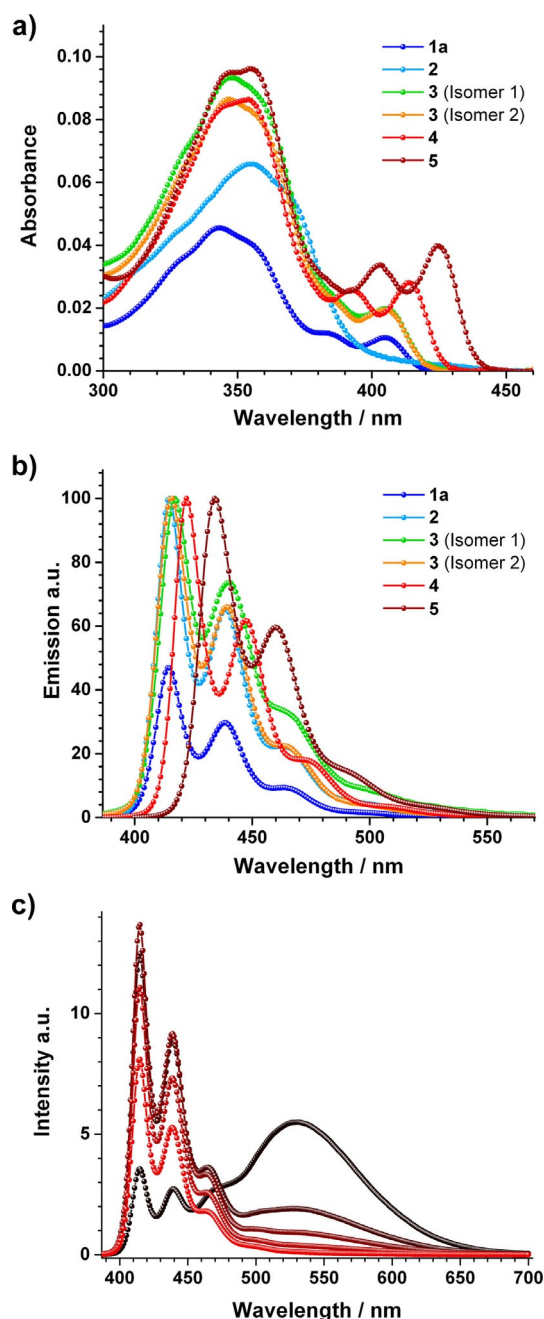


Figure 3. Absorption (a) and emission (b) spectra of compounds **1–5** from CH₂Cl₂ solutions. c) Emission spectra of **2** from CH₂Cl₂ solutions with an increasing concentration. Color scale from red to black.

i.e. 415, 438, and 463 nm (see Figure 3b and Table S5 in the Supporting Information), even though the calculated optical band gap for **1** and **2** differed significantly (Table S3 in the Supporting Information). This suggests that a) the excited state reached upon photoexcitation and emissive state are different and b) the emissive state is common for the latter diphosphahexaarene derivatives.

The emission spectrum of the quaternized derivative **4** in CH₂Cl₂ was in turn redshifted compared with **1** to 422 and 447 nm with a shoulder at 472 nm. In water, as for the absorption characteristics, the emission features remained almost un-

altered; i.e. that is, at 423, 447 nm. A stronger redshift was nevertheless observed for the borane adduct **5**, in consonance with its redshifted absorption features compared with **1**. Compound **5** emits with maxima at 434, 460, and 492 nm. Thus, the complexation of BCF to the phosphorus oxide moieties would modulate both the energy of the excited state reached upon photoexcitation and the emissive state.

Overall, analyses of the absorption/emission spectra unveiled relatively small Stokes shifts ranging from 458 cm^{-1} for compound **4** to 711 cm^{-1} for **3a,b** (Table S5 in the Supporting Information) and a Stokes shift of 4152 cm^{-1} for compound **2**.

On the other hand, experiments carried out by measuring the emission spectra at different concentrations revealed a particular scenario. Derivatives **1**, **3**, **4**, and **5** showed concentration-independent emission spectra. However, when increasing the concentration of the trivalent derivative **2**, the two emission maxima at 415 and 439 nm gradually faded while a new broad band at 527 nm emerged (Figure 3c). This band was found to revert upon dilution, recovering the original absorption spectrum. We hypothesize this band appeared owing to the formation of excimers. Six-membered phosphorus heterocycles with a trivalent λ^3 ; σ^2 -endo, σ^1 -exo atom possess one side of the scaffold with no out-of-plane substituents (the other side presents the out-of-plane phenyl ring), which would allow efficient face-to-face interactions. Thus, the 527 nm emission band would result from such an "aggregated" entity.

Finally, the fluorescence quantum yields (Φ) varied significantly as a function of the phosphorus functionalization (Table S5 in the Supporting Information). In CH_2Cl_2 , in agreement with the spectroscopic behavior observed earlier from trivalent phosphaphenylene derivatives,^[15] diluted solutions of the reduced species **2** featured only moderate quantum yields; i.e. $\Phi=10\%$. In contrast, the oxide derivatives **1**, possess high fluorescence quantum yields ($\Phi=81\text{--}84\%$).^[13] The thio-derivatives **3** emitted, in turn, with a low quantum yield of 1%. This is attributed to the typical heavy atom effect arising from the sulfur atoms as a result of a strong spin-orbit coupling, which leads to non-radiative decays through the triplet state. The quaternized derivative **4**, on the other hand, exhibited a fluorescence quantum yield as high as 80% in CH_2Cl_2 . In water, the photoluminescence of **4** remained significantly high ($\Phi=67\%$), which opens up new research opportunities as biomarkers. Finally, the coordination of the BCF to the phosphorus oxide centers slightly reduced the quantum yield to 78% compared with the parent compound **1**. These results corroborate the suitability of the phosphorus post-functionalizations to modify the physicochemical properties of diphosphahexaarenes.

Conclusions

In this article, we demonstrate that large linearly fused arenes based on six-membered phosphorus can be readily post-functionalized at the phosphorus atom. The phosphorus oxide derivatives can be furthermore quantitatively post-functionalized with the BCF Lewis acid. Overall, all post-functionalized diphosphahexaarenes are stable. Even though the reduced trivalent

derivative **2** and the borane adduct **5** are sensitive to oxidation/hydrolysis, they are, on the other hand, stable towards light and heat; i.e. they did not decompose under repeated cycles of illumination and heating. The thio-derivatives **3** and the quaternized species **4** are, in turn, stable towards air and moisture. All post-modified materials **2–5** dissolve in a variety of common organic solvents. Moreover, the diphosphahexaarenes **4** with two quaternized phosphorus centers are even soluble in highly polar solvents such as alcohols and water. DFT calculations revealed that the optical band gap is impacted by the phosphorus functionalization, although the oxidation of the trivalent phosphorus center with either oxygen or sulfur leads to practically the same band gap. However, the emission properties remained rather similar for the trivalent and pentavalent species, which points to a different nature of the first excited state that is reached upon photoexcitation and the emissive state. The stronger redshifted emission is reached by coordination of the BCF to the phosphorus oxide moieties. Finally, the fluorescence quantum yield of the diphosphahexaarenes is strongly impacted by the phosphorus functionalization. In CH_2Cl_2 , oxide and quaternized derivatives emit with fluorescence quantum yields around 80%, whereas trivalent species and the sulfur derivatives emit with $\Phi=10\%$ and 1%, respectively. In water, the quaternized diphosphahexaarene exhibits a fluorescence quantum yield of 67%.

Based on our results, we envisage the use of the diphosphahexaarenes as building blocks to construct superior architectures through phosphorus post-functionalization and the investigation of the water-soluble derivatives as biomarkers. The utilization of the phosphorus-modified systems into organic electronics and further spectroscopic investigations on the particular behavior of **2** are currently underway.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: borane coordination · diphosphahexaarenes · phosphorus heterocycles · post-functionalization · stability

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