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Tetracationic phosphonium-bridged ladder stilbenes: redox states and electronic properties of highly charged P-heteropolycyclic materials

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This work describes the development of an air-stable tetracationic P-heteropolycyclic material in which four phosphorus atoms are incorporated into an extended π -conjugated framework. The system, which may be viewed as a doubly phosphonium-bridged ladder stilbene, was found to display a rich redox chemistry and charge-dependent interaction with DNA.

Redox-active organic molecules with a range of specifically accessible oxidation states are of fundamental interest in the development of new and readily processible functional materials.^{1–4} In this context, polycyclic π -conjugated frameworks are capable of accommodating multiple charges while maintaining structural integrity and provide access to materials which are relevant for organic electronic and optoelectronic applications.^{1,5–15}

From a practical point of view, the materials employed in such applications ideally require chemical robustness under ambient conditions.^{2,8,11,16} Air stability and water solubility^{13,17} are among the critical properties, especially for emerging biological and biomedical applications where oxidative stress and aqueous media impose stringent stability requirements.^{18,19}

Beyond the extensive chemistry of N-heteropolycycles,^{20–24} the integration of other main-group elements into π -conjugated systems has emerged as a powerful strategy to access unusual electronic configurations and a rich redox chemical behaviour.^{1,7–9,11,16,25–29} Notable examples include the isolation of neutral, radical, and biradical states in diboraindeno[1,2-*b*]fluorene derivatives, demonstrating that heteroatom frameworks can stabilize multiple oxidation states within a molecular scaffold.³⁰ Related concepts were introduced earlier by Yoshifuji, who reported the first synthesis and comprehensive characterization of diphosphaquinones and diphosphathienoquinones,

compounds that exhibit pronounced redox activity associated with their quinoidal π -systems.³¹

Despite these advances, highly charged phosphorus-containing π -systems remain rare, and systematic strategies to increase charge density while simultaneously maintaining air stability and aqueous compatibility³² are still limited. In this context, we set out to extend ladder-type structures by increasing the number of cationic phosphorus centres within a single conjugated framework. Whereas Yoshifuji's diphosphaquinones are intrinsically limited to dicationic species, incorporation of four phosphorus atoms would enable access to a tetracationic material with substantially increased charge density.

In previous work,^{4,32} we investigated π -extended dicationic phosphonium-bridged ladder stilbenes. Notably, these exhibited both water solubility and air stability. Among these, one of the naphtho-annulated derivatives was found to undergo a competing transformation, generating an unprecedented bis(Δ^2 -phosphetene) dication (Fig. 1).³²

To construct a bidirectional phospholo[3,2-*b*]phosphole framework and to suppress the potential formation of a bis(Δ^2 -phosphetene) structure, a linear substitution pattern was therefore selected for the present study.

The first precursor (**1**) was synthesized in two steps from 1-bromo-2-iodobenzene (see Scheme 1), while the second precursor (**2**) was obtained in a five-step synthesis, both using well established synthetic methods (see SI for details). Sonogashira couplings of these precursors with 1,4-dibromo-2,5-diiodobenzene yielded compounds **3**³³ (70%) and **4** (71%). After *in situ* lithiation with *tert*-butyllithium and subsequent treatment of the lithiated intermediates with ClP(^tPr)₂, the tetraphosphine targets **5** and **6** were obtained in high yields (73% and 70%). In contrast to the diphosphines reported in our previous work,³² the tetraphosphines **5** and **6** could be isolated and fully characterized, despite their pronounced sensitivity towards air and their thermal lability. The ³¹P{¹H} NMR spectra display two singlet resonances for each compound (δ = 4.9 ppm, 3.0 ppm for **5**; 10.0 ppm, 4.0 ppm for **6**, see SI).

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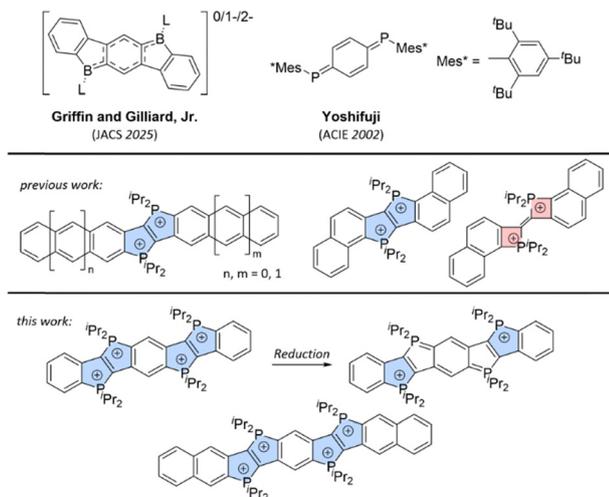


Fig. 1 The focus of previous work was the synthesis of π -extended phospholo[3,2-*b*]phospholes,^{4,32} while this study presents the extension of the π -system via a bidirectional extension of the phospholo[3,2-*b*]phosphole motif. Structurally related diboraindeno[1,2-*b*]fluorene derivatives³⁰ (Griffin and Gilliard, Jr.) and diphosphaquinones³¹ (Yoshifuji) are shown above.

In the subsequent oxidation and cyclization, **5** and **6** were treated with C_2Br_4 in dichloromethane at -40°C and then warmed to room temperature, which afforded the tetracationic P-heteropolycycles **7** and **8** as bromide salts. These were isolated as bright orange-red powders in moderate yields (62% and 61%) by filtration. Compounds **7** and **8** give yellow and orange solutions, respectively (Scheme 1). The UV/Vis absorption spectra display similar features (see SI). However, the absorption bands of **8** are bathochromically shifted relative to those of **7**. This trend is consistent with the increased π -conjugation in **8** and is in agreement with previous observations for dicationic phosphonium-bridged ladder stilbenes.³² The lowest-energy absorption maximum of **8** (530 nm) is red-shifted by 42 nm compared to **7** (488 nm), whereas the higher-energy absorption bands show smaller shifts of approximately 10 nm (351 and 272 nm for **7**, compared to 360 and 283 nm for **8**).

The oxidized products exhibit two doublets in the $^{31}\text{P}\{\text{H}\}$ NMR spectra ($\delta = 63.0$ ppm, 60.7 ppm for **7**; 62.8 ppm, 58.2 ppm

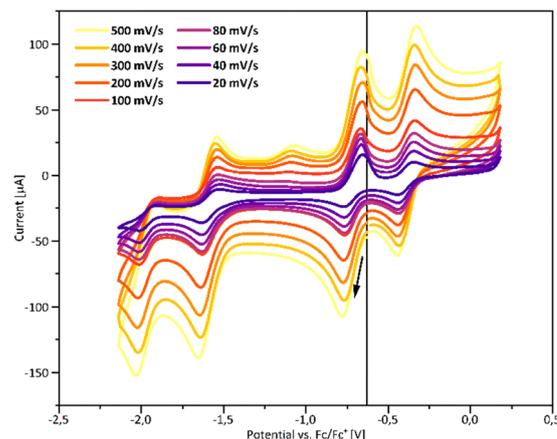
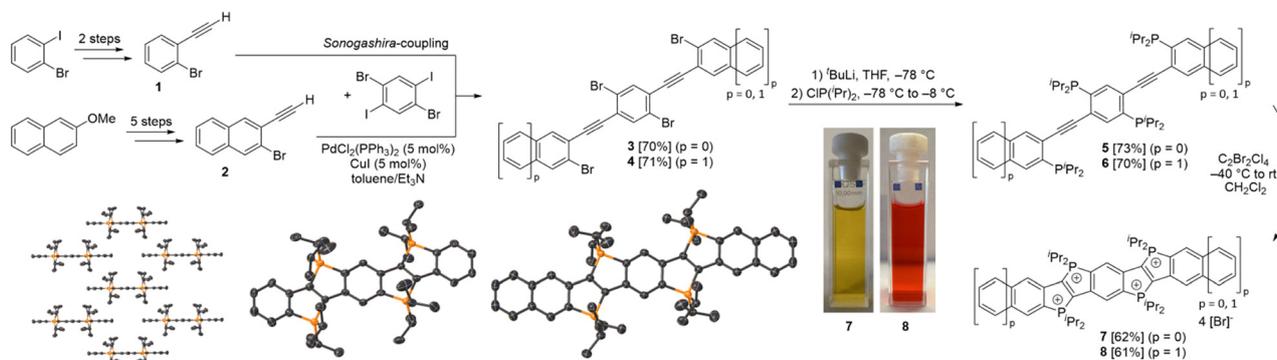


Fig. 2 Cyclic voltammogram of **7** in MeCN, supp. electrolyte Bu_4NOTf (0.1 M), reference Fc/Fc^+ (black vertical line and black arrow indicate the start and direction of scans).

for **8**). Both compounds were found to be air-stable for several weeks and could be purified by recrystallization from $\text{MeOH}/\text{Et}_2\text{O}$. Their crystal structures established almost planar polycyclic π -systems with the iso-propyl groups pointing above and below the plane, thereby shielding the π -system laterally.

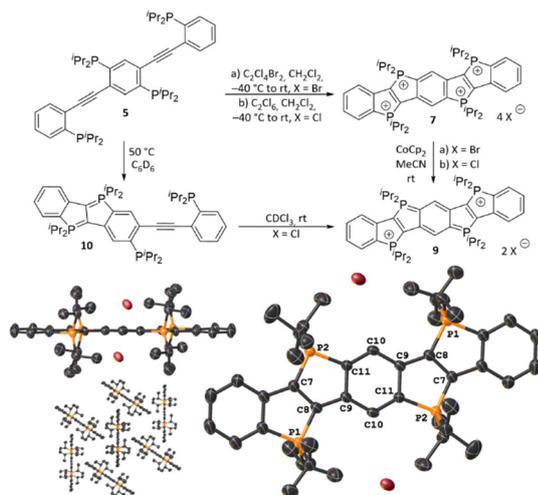
The redox behaviour of **7** and **8** was investigated by cyclic voltammetry. Three quasi-reversible and one irreversible reduction waves were observed for **7** (Fig. 2). Initiating the scan at 0 V vs. Fc/Fc^+ and observing no current at the starting potential allows the redox wave at $E_{1/2} = -0.39$ V to be assigned to a reduction process (see SI for further details). The irreversible reduction wave at $E = -2.02$ V is most likely due to ring-opening. In contrast, for compound **8** a series of weak and irreversible redox features were found, suggesting decomposition (see SI for spectrum and further details). This observation is consistent with the reduced stability of **8** compared to **7**, as observed in ctDNA interaction experiments.

Based on these findings, the isolation of reduced states of compound **7** was targeted. The dication **9** could be obtained by two synthetic routes: (i) reduction of the tetracation **7**, and (ii) oxidation of semicyclic neutral *P*-diylide precursor **10** (Scheme 2). The latter was obtained by heating **5** in solution



Scheme 1 Synthesis of **7** and **8** and the crystallographically determined structures of **7** and **8** (co-crystallized and disordered solvent molecules, bromide counter ions, and hydrogen atoms omitted for clarity, thermal ellipsoids drawn at the 50% probability level).





Scheme 2 Synthesis of **9** via two different routes: oxidation of **10**, or reduction of **7**. The crystallographically determined molecular structure of **9** indicates decreased aromaticity in the central benzene unit (co-crystallized solvent molecules and hydrogen atoms omitted for clarity, thermal ellipsoids drawn at the 50% probability level).

for 5.5 hours, whereas the corresponding doubly cyclized *P*-diylide was not detected even for higher temperatures, longer reaction times, or alternative solvents, all of which resulted in decomposition of the starting material. Oxidation of **10** with CDCl_3 afforded the air-sensitive dication **9**, while reductive conversion of tetracation **7** was achieved by treatment with CoCp_2 in acetonitrile at room temperature. As to be expected for a quinoidal structural unit, the bond lengths in the central ring ($d_{\text{C}_9\text{-C}_{10}} = 1.401(3) \text{ \AA}$; $d_{\text{C}_9\text{-C}_{11}} = 1.452(3) \text{ \AA}$; $d_{\text{C}_{10}\text{-C}_{11}} = 1.381(3) \text{ \AA}$) deviate from the typical C–C bond length in benzene (1.397 \AA).³⁴ In contrast, the bond lengths of the tetracation **7** ($d_{\text{C}_9\text{-C}_{10}} = 1.387(9) \text{ \AA}$; $d_{\text{C}_9\text{-C}_{11}} = 1.389(8) \text{ \AA}$; $d_{\text{C}_{10}\text{-C}_{11}} = 1.418(10) \text{ \AA}$) are more evenly distributed and thus more consistent with the assigned benzene-like electronic structure. Additionally, a deviation from a typical P–C single-bond length (*ca.* 1.85 \AA)³⁵ is observed for dication **9** ($d_{\text{P}_2\text{-C}_{11}} = 1.793(2) \text{ \AA}$ and $d_{\text{P}_2\text{-C}_7} = 1.758(2) \text{ \AA}$). In contrast, in tetracation **7** the P2–C7 bond ($1.817(7) \text{ \AA}$) is notably longer than the P2–C11 bond ($1.792(2) \text{ \AA}$).

NICS(1_{zz} -XY scans (nucleus-independent chemical shifts)^{36,37} of **7** and **10** (Fig. 3) support this observation and, in particular, suggest that the dicationic phospholo[3,2-*b*]phosphole core (b, b*, c and c* rings) of **7** is electronically decoupled from the annulated arene rings on the sides. This is consistent with the findings of our previous studies of π -extended dicationic phosphonium-bridged ladder stilbenes³² which also showed that the small positive NICS(1_{zz}) values for the 5-membered rings are not indicative of antiaromaticity³⁸ but similar to those of a constrained *trans*-stilbene.³²

Anisotropy of the induced current density^{39,40} (ACID) plots were computed to visualize the magnetic response of the π -system (Fig. 3). For compound **7**, the current-density vectors within the central ring are oriented clockwise, thereby indicating a diatropic ring current (red circular arrows). In contrast, compound **10** exhibits current-density vectors of the central

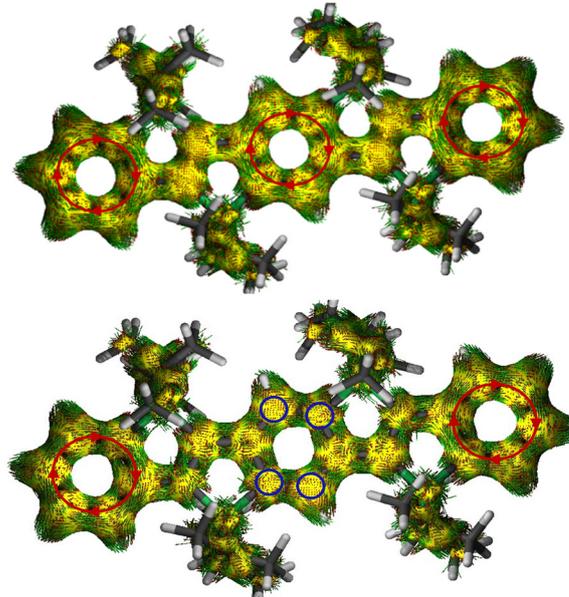
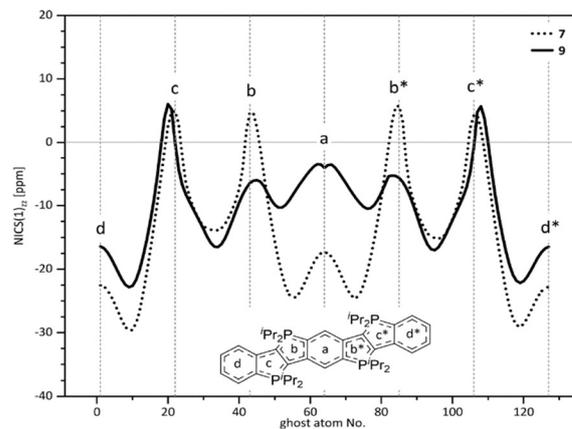


Fig. 3 Top: NICS(1_{zz} -XY^{36,37} scans for **7** and **9** in comparison (B3LYP, def2-TZVPP, D3BJ, CPCM for CH_2Cl_2),^{41–49} starting in the centre of (d). Bottom: Anisotropy of the induced current density^{39,40} (ACID) plots for **7** (top) and **9** (bottom) in comparison (B3LYP, def2-TZVPP, GD3BJ, SCRF for CH_2Cl_2 , isovalue = 0.05 (default), see SI for further details).^{41–48}

ring directed towards the observer (blue circles), consistent with a substantially reduced diatropic contribution. The calculated attenuation of the diatropic ring current correlates well with the NICS(1_{zz}) values and the crystallographically determined bond-length pattern.

With the aim of generating the radical mono- and trications related to **7** and **9**, the precursor **5** was reacted with, respectively, one and three molar equivalents of ferrocenyl chloride. While attempts to isolate these radical cations were unsuccessful, the formation of the radical trication was confirmed *in situ* by EPR spectroscopy (Fig. 4 and SI for further details).

Charged heteropolycyclic compounds have found applications as DNA-intercalators,^{50–52} and it was thus of interest to probe the interaction of the previously published dicationic phosphonium-bridged ladder stilbenes as well as the newly obtained tetracations with DNA. The two dicationic reference compounds represented in Fig. 5 provided relevant benchmarks



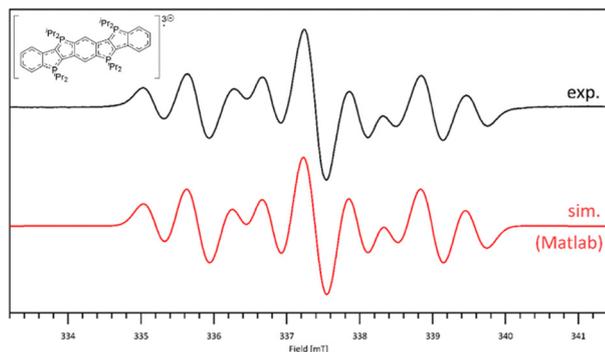


Fig. 4 Experimental and simulated EPR spectra obtained after reaction of **5** with 3 eq. $[\text{FeCp}_2]\text{Cl}$ or 3 eq. Ph_3CCl , in CH_2Cl_2 at rt.

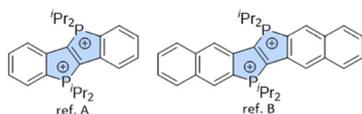


Fig. 5 Previously published reference systems for benchmark of ctDNA intercalation with tetracations.^{4,32}

in this context.^{4,32} Linear dichroism⁵³ (LD) spectroscopy was performed to evaluate their non-covalent interaction with DNA. Whereas compound [ref. **A**]²⁺ showed no evidence of intercalation, probably due to insufficient π -extension, compound [ref. **B**]²⁺ exhibited clear spectroscopic signatures of DNA intercalation while maintaining good solution stability, demonstrating that effective DNA binding requires a balanced combination of π -extension, charge state, and aqueous stability (see SI for spectra and details).

Subsequently, the tetracationic ladder stilbene **7** was tested. Measurements showed no negative LD signal at the absorption wavelength of the compound, indicating the absence of DNA intercalation,⁵³ in good agreement with [ref. **A**]²⁺ with the same extent of π -extension. The correlated decrease of the ctDNA LD band at ca. 260 nm suggests DNA coiling induced by electrostatic interactions rather than π - π intercalation.⁵⁴ Compound **8** intercalates into DNA when mixed with ctDNA immediately after dissolution in pure water but its rapid decomposition in aqueous media in the absence of DNA precludes any reasonable application as intercalator. Overall, these preliminary results show that, in contrast to the dicationic reference [ref. **B**]²⁺, the tetracationic ladder stilbenes are not suitable as DNA intercalators. Insufficient π -extension, limited aqueous stability, and possibly excessive charge density appear to prevent sustained DNA binding.

In summary, the targeted synthesis of the tetracationic ladder stilbenes reported herein establishes a versatile molecular platform for π -extended, redox-active phosphorus-containing systems with exceptionally high charge density. Ongoing efforts are directed toward further structural modification to enhance redox stability and environmental compatibility, with potential applications in redox catalysis^{6,55} particularly as redox mediators.^{12,56–58}

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: experimental details, NMR spectra, computational data, details on ctDNA-intercalation measurements, electrochemical measurements, crystallographic data. See DOI: <https://doi.org/10.1039/d6cc00544f>.

CCDC 2525134–2525136 contain the supplementary crystallographic data for this paper.^{59a–c}

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