

From Aqua Green to Deep Red in One Step: Targeted Design of a Highly Luminescent Phosphacyclic Vat Orange 3 Dye

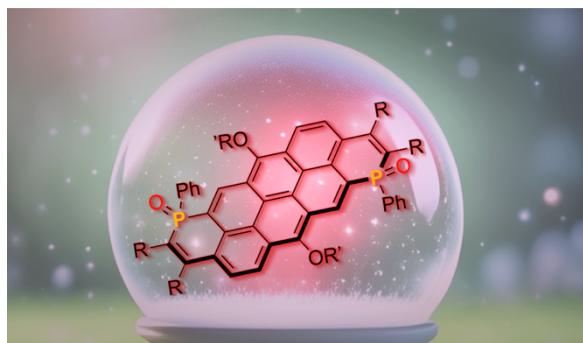
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Supporting Information Placeholder



ABSTRACT: Silver-mediated phosphacyclic ring expansion with strategic placement of phosphorus and dimethyl acetylenedicarboxylate (DMAD) on Vat Orange 3 was carried out. The target compounds possess narrow HOMO-LUMO energy gaps as low as 2.02 eV, with pronounced absorption across the visible region of the optical spectrum and intense luminescence at 691 nm with impressive quantum yields of up to 70%. Moreover, the P-based conjugated materials exhibit reversible reduction events as low as -0.98 V.

Red luminescent materials have gained widespread utility in bioimaging, photodynamic therapy,^{1–3} and materials science (OLEDs, sensors).^{4–6} While reports on efficient red-light emitters have been steadily increasing in recent years, maintaining intense fluorescence remains challenging, as it shifts into the deep-red region (650–700 nm). This is attributed to increasing non-radiative decay processes as the energy difference between the excited and ground states narrows,⁷ and this is further exacerbated in the near-IR (NIR) region.^{8,9} As a result, organic conjugated systems capable of achieving quantum yields above 40% in these regions remain scarce, despite being highly advantageous for a variety of applications.^{10–12} Designing conjugated materials with tailored luminescence features therefore continues to be an active area of research.

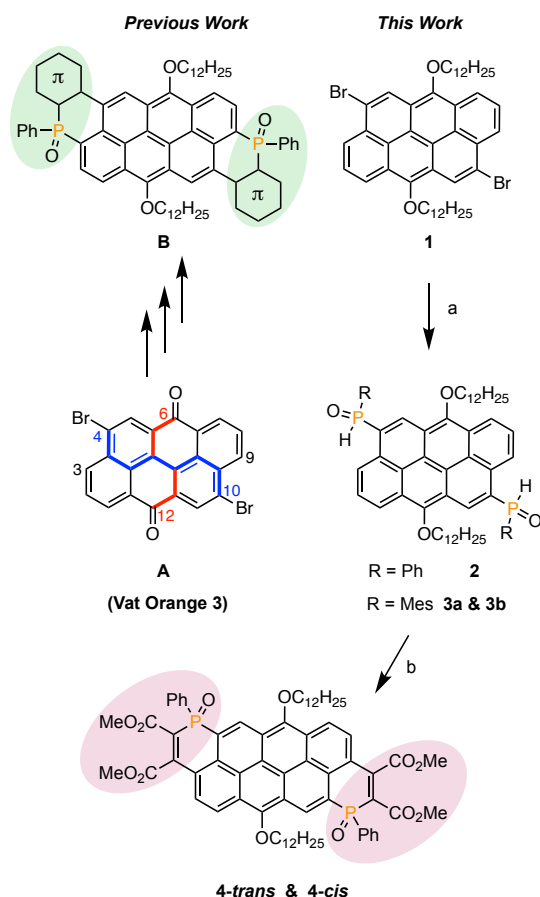
Vat dyes are a distinct class of polyaromatic hydrocarbons with a long history in the textile industry owing to their intense absorption in the UV-vis region and resulting vibrant colors.¹³ Among them, Vat Orange 3 (VO3, **A**, Scheme 1) has proven to be a valuable building block for conjugated materials with notable functional properties, such as pronounced luminescence. The key to activating luminescence in VO3-based scaffolds lies in precise functionalization of the sites bearing the keto and bromo functional groups.^{14,15} Furthermore, embedding phosphorus into the backbone of π -conjugated structures is a versatile tool to tailor the overall electronics of organic

systems. Studies suggest that this effect is largely governed by the interactions between external P-substituents and the π -conjugated system in the P-heterocycle, typically resulting in a lowered lowest unoccupied molecular orbital (LUMO).^{16,17} Indeed, numerous examples of phosphorus-containing conjugated materials with advanced light-emitting and electron-acceptor behavior—developed by us and other groups—are well documented in the literature.^{16,18–20} Our initial study on phosphorus-modified VO3 led to a series of conjugated materials (**B**, Scheme 1) with highly tunable optical and electrochemical properties via phosphorus modification.²¹ The phosphorus moieties installed at the 3 and 9 positions of VO3 (Scheme 1) have a pronounced impact on the optical and electronic properties of the inherently green-emissive framework, despite the small phosphorus-to-hydrocarbon ratio within the scaffold.

Conversely, the majority of reported core-substituted VO3 derivatives confirm that modulation of the frontier molecular orbital (FMO) energy values are more substantial when substituents are installed along the 6–12 and 4–10 conjugation pathways (Scheme 1).^{22,23} Consequently, we envisioned that placing phosphorus at the 4 and 10 positions would exert a more pronounced stabilizing effect on the LUMO energy level, thereby effectively decreasing the energy gap. To ensure the success of this approach, we selected dimethyl acetylenedicarboxylate (DMAD) as the ring-expanding partner, as

its electron-withdrawing ester groups were expected to further lower the LUMO energy level and shift the emission of the scaffold well into the red region and beyond (**4**, Scheme 1).

Scheme 1. Previous and current target structures along with the attempted synthetic route.



1: *n*-BuLi, PhPCl₂ (MesPCl₂ for **3**), THF, 6h; **2:** H₂O 1h (70 %). (**b**) Ag₂O, DMAD, CH₃CN, 100 °C, overnight (17 %).

The synthetic strategy toward **4-trans** and **4-cis** (defined by the stereochemistry of the two P-centers) involves precursor **1**²¹ that enhances the solubility of genuine VO3 and also suppresses side reactions involving the keto groups. Lithiation of **1** with *n*-BuLi, followed by addition of PhPCl₂ for the direct attachment of PhPCl-moieties to the main framework was explored. Due to the low solubility of **1** in THF at -78 °C, the reaction mixture was stirred at elevated temperatures for an extended period after addition of *n*-BuLi at low temperature, to ensure complete lithiation. Optimization of this step, followed by hydrolyzation of the PhPCl moieties and rearrangement into the PhP(O)H functional groups provided **2** in up to 70% at a gram scale. Interestingly, the ³¹P{¹H} NMR spectrum of **2** revealed two barely resolved singlets at δ³¹P: 25.3 and 26.0 ppm suggesting of the presence of diastereomeric species that could not be separated. To confirm this assumption, variable-temperature ³¹P{¹H} NMR spectroscopy was performed on **2**, revealing the coalescence of the two singlets at 100 °C and re-emergence of the original signals upon cooling (Figure S1). To isolate the isomers, we surmised increasing the sterics around the P-center would be beneficial. Indeed, using mesityl group instead of phenyl on the phosphorus, rendered the separation of the diastereomers of **3** possible. The blue luminescent

compounds **3a** and **3b** were separated using column chromatography (CHCl₃:acetone-10:0.8) with ³¹P{¹H} NMR shifts at 11.2 and 11.1 ppm.

Ag-mediated oxidative coupling^{24,25} between the phosphorylated **2** and DMAD led to the formation of phosphacycles on each side of the framework. Due to the radical nature of the reaction, the target species **4** was afforded as mixture of the two possible isomers with *trans*- and *cis*-configured P-Ph groups with respect to the plane of the conjugated scaffold. Both isomers are deep blue in solution and the solid state, indicative of a reduced energy gap, but highly stable under ambient conditions. We were able to separate **4-trans** and **4-cis** through column chromatography (CHCl₃:acetone-10:1) and the species were characterized by respective singlets at δ³¹P: 6.9 and 6.8 ppm and their corresponding ¹H and ¹³C{¹H} NMR spectra.

Single crystals of **4-trans** were grown from acetone that confirmed the structural attributes of this *meso* species via X-ray diffraction (Figure 1). Contrary to **B**,²¹ the fused scaffold of **4-trans** is entirely flat, i.e., with the merged phosphacycles deviating only 1° from planarity, suggesting effective conjugation throughout the π-system. The terminal ester groups proximal to the phosphorus centers are coplanar and consequently involved in conjugation, while the distal ester groups are perpendicular to the main scaffold, likely due to steric pressure. Furthermore, the packing in the solid state (Figure S4) shows isolated slipped stacks in an overall herringbone pattern without any π-stacking interactions. As in our previous P-modified VO3 species **B**, the extended π-systems are separated by intercalated dodecyl chains from neighboring molecules in a different stack.

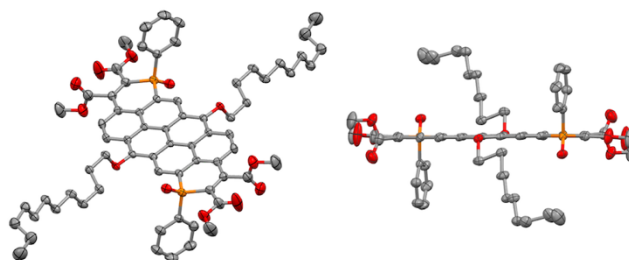


Figure 1. Different views of **4-trans** in the solid state (ellipsoids at 50% probability, H atoms omitted for clarity).

However, it should be noted that the reaction also provided a significant number of difficult-to-separate byproducts, requiring the optimization of the reaction conditions (see SI), that ultimately improved the yield to 17% overall using CH₃CN as solvent at 100 °C. Isolation of some of the purple byproducts from the reaction mixture by preparative thin layer chromatography (TLC) revealed their identity as partially ring-closed species **C** and **D** using HRMS (Figure S2).

Furthermore, we presumed that the ring closure could also occur on the exocyclic P-Ph (**E**, Figure S2) adding to the complexity of this reaction. The Mes-P moieties in compound **3** were expected to block the active positions on the exocyclic substituent and the ring closure was thus attempted with **3** as well. Unfortunately, this strategy did not result in the desired outcome, rather leading to an even more complex mixture (Figure S3), which is probably due to ineffective production of the P-centered radical or its ineffective attack on DMAD due to the increased steric profile of Mes vs. Ph.

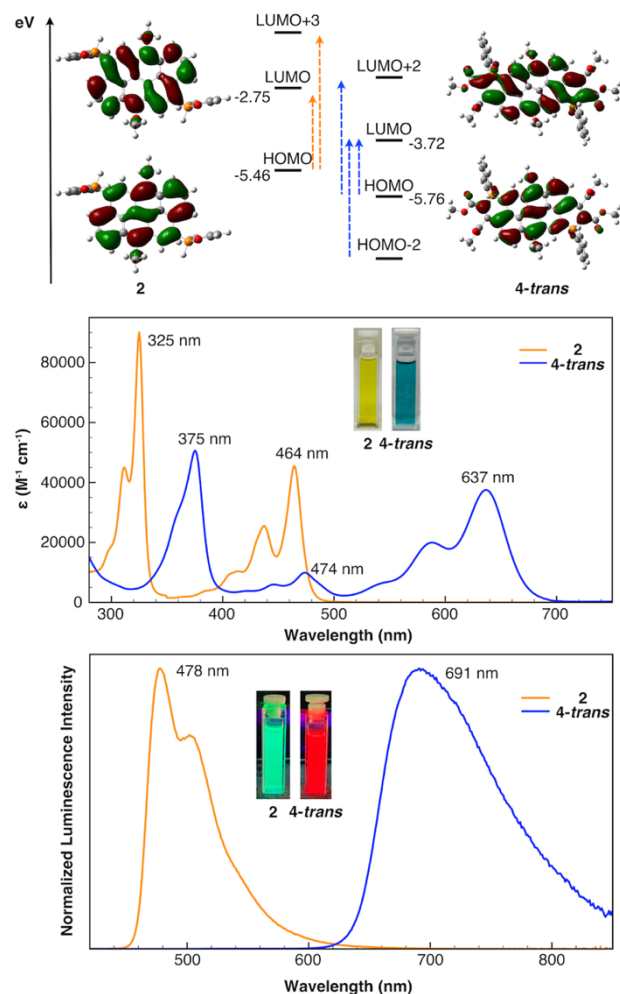


Figure 2. FMOs along with the involved electronic transitions (top), absorption (middle), and emission (bottom) spectra of **2** and **4-trans** in CH_2Cl_2 .

DFT calculations at the B3LYP/6-31+G(d) level of theory confirmed involvement of the entire conjugated core in the π -system across all synthesized species. Moving from **1** to **2**, only a minimal stabilization effect from the phosphoryl groups on the LUMO was noted ($-2.64 \rightarrow -2.75$ eV). While the small influence can be linked to the electron-accepting nature of the phosphoryl groups, the limited conjugation between phosphorus and the π -system suggests only a modest effect (Figures S6 and 2, top). However, stark differences are observed after ring closure; in **4-trans** (and **4-cis**), the P-center shows significant contribution to the LUMO, and participation of the adjacent ester groups is also evident (Figure 2, top). This stabilizes the LUMO substantially—from -2.75 to -3.72 eV—along with a lesser impact on the HOMO level. This decreases the overall FMO energy gap from 2.71 eV in **2** to 2.04 eV in **4-trans**, highlighting the effectiveness of the employed strategy (see Figure S6 for other precursors and isomers).

The photophysical properties of the synthesized species were investigated in dichloromethane (see SI). Both **1** and **2** exhibit two distinct absorption bands around 320 and 460 nm, respectively, red-shifted by only 5 nm from **1** to **2**, as supported by DFT (Figure S7). Furthermore, the extinction coefficients of both compounds exceed $90,000 \text{ M}^{-1} \text{ cm}^{-1}$, confirming the significant absorption features of

vat-dye-based scaffolds. Notably, the absorption spectrum of **4-trans** (similar to **4-cis**) is comprised of three sets of bands around 375 , 474 , and 637 nm, respectively, featuring light-absorption that covers the entire visible region and extending into the UV (Figure 2, middle). Comparison between **2** and **4-trans** confirms that the phosphacycles induce a remarkable red-shift of 173 nm for the low-energy absorption ($464 \rightarrow 637$ nm) that is achieved with a relatively small structural change. The extinction coefficients for **4-trans** are up to $50,600 \text{ M}^{-1} \text{ cm}^{-1}$ with a strong absorption beyond 600 nm that makes it a potential conjugated material for photovoltaics. It is worth noting that the optical properties of diastereomers **3a** and **3b** are nearly identical and resemble that of their phenyl congener **2**, which is expected given the structural similarity among these species (Figure S8).

To obtain deeper insight into the nature of the observed absorption features, time-dependent TD-DFT calculations were performed that align well with the experimental data. The low-energy bands for both **2** and **4-trans** are results of HOMO $\rightarrow$ LUMO transitions ($\pi \rightarrow \pi^*$) with respective oscillator strengths of $f = 0.45$ and 0.74 , confirming the intense absorption in the red-shifted area (Figure 2, top). The high-energy features can be attributed to a combination of transitions, with the most significant contributions arising from HOMO $\rightarrow$ LUMO+3 for **2**, and HOMO $\rightarrow$ LUMO+2 for **4-trans** with $f = 0.61$ and 0.85 . The emerging third absorption band for **4-trans** (474 nm) receives a strong contribution from HOMO-2 $\rightarrow$ LUMO with $f = 0.30$ (see Figure S6 for other species).

The small red-shift in the emission between **1** and **2** ($470 \rightarrow 478$ nm) is due to the largely unaffected electronics in these systems (Figure S7). However, replacing bromine in the weakly emissive **1** with P-based moieties in **2** results in a drastic increase in quantum yield (QY; **1**: 2% vs. **2**: 56%), due to the suppression of non-radiative relaxation pathways; this is an established effect of phosphoryl moieties in organic materials.²⁶ Compounds **4-trans** and **4-cis** exhibit a surprisingly large red-shift of 213 nm for their emission maxima at 691 nm—at the trailing edge of the deep-red region—that is accomplished through a single synthetic step (Figures 2, bottom and S7). Moreover, the emission profile expands into NIR region, progressing past 800 nm. Impressively, **4-trans** and **4-cis** are strongly luminescent, with QY values of up to 70%. This is rare for compounds (organic and inorganic) emitting in this spectral region, supporting its high value for applications in biological and materials sciences.

Positive solvatochromism was representatively confirmed for **4-trans** (see Figure S9). In less polar solvents such as pentane and diethyl ether, **4-trans** exhibits blue-shifted emissions at 634 and 650 nm, respectively (Table S4). More polar solvents and those capable of hydrogen bonding, such as acetone and methanol, red-shift the emission to 700 and 732 nm, respectively. The overall emission range across the solvents tested reaches an impressive value of almost 100 nm. In methanol, most of the emission profile of **4-trans** notably falls into the NIR region, with a relatively high QY of 16%. A similar positive solvatochromism is observed in the absorption spectra, albeit with less pronounced shifts overall (Table S4).

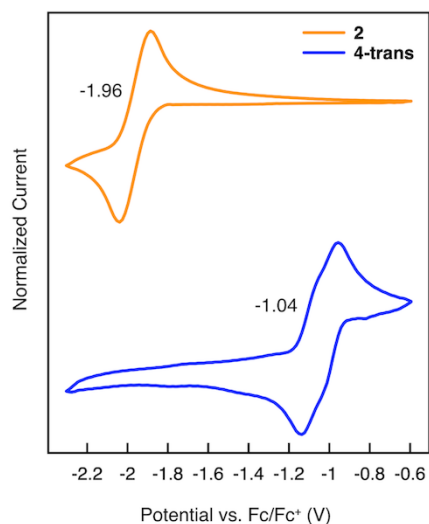


Figure 3. Cyclic voltammograms (IUPAC) of **2** and **4-trans** in CH_2Cl_2 ; scan rate: 100 mVs^{-1} , $0.1 \text{ M } n\text{-Bu}_4\text{PF}_6$, vs. Fc/Fc^+ , starting potential: -0.6 V , reductive scans.

Given the beneficial electrochemical properties of our previous phosphorus-modified VO3 species **B** with reversible reductions at -1.7 and -2.0 V (vs. Fc/Fc^+) respectively,²¹ cyclic voltammetry was conducted on the new species as well (Figure 3). The voltammogram of **2** shows a fully reversible reduction peak at relatively high potential of -1.96 V (vs. Fc/Fc^+) that is likely comprised of a one-step two-electron reduction process (due to the presence of two P-components).²¹ As the LUMO energy level experiences a meaningful decrease in **4-trans**, the reduction events undergo a substantial potential shift to -1.04 V (vs. Fc/Fc^+) while retaining their reversibility, confirming the high stability of these species upon electron uptake. However, the two reduction events appear at slightly different potentials, as the reduction events in **4-trans** begin to show signs of separation, supporting electronic communication across the scaffold. This phenomenon is more pronounced in **4-cis**, as the reduction events occurring at -0.98 and -1.11 V (Figure S10) are fully resolved, with a center aligning with the reduction feature of **4-trans**. Also, the new species exhibit no reversible oxidation, which is a common observation for such species (Figure S11).²¹

In summary, we successfully developed a ring-fusion methodology for diminishing the LUMO level and narrowing the FMO energy gap of the VO3 scaffold using phosphoryl and alkyne building blocks. The resulting phosphacyclic materials experience an almost 1 eV reduction for their energy gap in one synthetic step. The absorption features disclose intense absorption throughout the visible spectrum especially past 600 nm . More impressively, the new species turned out to be high-performing luminescent emitters with quantum yields of up to 70% and pronounced positive solvatochromism in the red-NIR region. The new functional materials also exhibit enhanced electron-accepting properties with low reduction thresholds that confirm the potentially broad utility of these species in materials chemistry.

ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

Experimental details; ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of all new compounds; X-ray crystal data, structure refinement and selected bonds and angles for **4-trans**; absorption and emission spectra, cyclic voltammograms, and computational data. The Supporting Information is available free of charge on the ACS Publications website.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. Author contributions are as follows: R.D.: formal analysis, investigation, methodology, visualization, writing – original draft; H.L., S.A., A.B., and J.L.: formal analysis, investigation; A.A.: investigation, resources; C.R.N., T.B.: conceptualization, funding acquisition, validation, project administration, writing – review and editing.

Notes

The authors declare no competing financial interest.

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