Cationic Organophosphorus Chromophores: A Diamond in the Rough among Ionic Dyes

Andrey Belyaev,*[a] Pi-Tai Chou,*[b] and Igor O. Koshevoy*[a]
Abstract: Tunable electron-accepting properties of the cat-
ionic phosphorus center, its geometry and unique prepara-
tive chemistry that allows combining this unit with diversity
of \( \pi \)-conjugated motifs, define the appealing photophysical
and electrochemical characteristics of organophosphorus
ionic chromophores. This Minireview summarizes the
achievements in the synthesis of the \( \pi \)-extended molecules
functionalized with P-cationic fragments, modulation of their
properties by means of structural modification, and empha-
sizes the important effect of cation-anion interactions, which
can drastically change physical behavior of these two-com-
ponent systems.

1. Introduction

Charged organic molecular chromophores demonstrate re-
markably diverse photophysical and electrochemical proper-
ties, which have been utilized in a wide range of photonic ap-
lications. Due to the ionic nature, many fluorophores (e.g. cy-
anines, squaraines, rhodamines etc.) have appreciable solubility
in protic solvents, and therefore serve as bioimaging agents
and chemosensors in physiologic medium.[1] Cationic com-
 pounds, which typically incorporate quaternized pyridyl motifs
(i.e. viologen-type species), undergo redox reversible processes
and play a key role in the development of electro/fluorochro-
mic devices.[2] Furthermore, involvement of charged \( \pi \)-conju-
gated molecules in non-covalent (ion-\( \pi \)-electrostatic) interac-
tions can substantially affect optical properties of the system
and has been actively employed in the design of stimuli-res-
sponsive and smart molecular materials.[3] For instance, intra-
and intermolecular cation(\( \pi ^{-} \))–\( \pi \) stacking comprising pyridi-
um units has proven to be an efficient approach to enhance
fluorescence in solution and in solid, representing a paradigm
for switchable luminescence signaling.[4] Ionic dyes, as two-
component salts, are capable of undergoing non-innocent
cation-anion interactions in aggregated or non-dissociated
(close or contact ion pair) states. Already in the 80’s it was not-
ticed that the formation of ion pairs in the solvents of low po-
larity influences the absorption spectra of ionic chromo-
ophores,[5] pointing to the ground state aggregation. Intuitively,
similar association effects might be expected in the excited
state, thus modulating the emission characteristics of ionic
fluorophores. Despite of this intriguing feature, very limited ex-
perimental and theoretical data have been reported in relation
to the excited state dynamics of ion pairs during the last decade.[6]

The field of ionic dyes has been dominated by nitrogen- and
oxygen-containing organic compounds. The heavier pnictogen
homologue, phosphorus, has received considerably less sys-
tematic attention as positively charged electron deficient
center (\( \chi ^{2} + \sigma ^{-} \) or \( \chi ^{2} \sigma ^{-} \)) within the \( \pi \)-conjugated chromophore
motif, albeit cationic organophosphorus species (mostly phos-
phonium salts) have long been investigated and applied in or-
ganic synthesis, catalysis, and biomedicine.[7] In contrast to P-
cationic photofunctional organic compounds, the P-neutral
congeners (primarily \( \chi ^{2} + \sigma ^{+} \) chalcogenide derivatives of tertiary
phosphines and P-heterocycles) have been a subject of thor-
ough investigation,[8] particularly as promising materials for
opto-electronic devices (light-emitting diodes and solar cells)
that was a central topic of a number of detailed reviews.[9]

In this respect, herein we mainly focus on the preparation
and the properties of the chromophore molecules with the
phosphorus-containing cationic groups attached to or integrat-
ed in a \( \pi \)-conjugated scaffold, where they can act as electron-
accepting components having a distinct impact on the photopho-
ysical or electrochemical behavior. Thus, compounds bear-
ing remote phosphonium groups linked via aliphatic spacers
(e.g. mitochondrial probes[10]), or ionic liquids with non-chro-
mospheric phosphonium cations[11] are out of the scope of this
work.

2. Acyclic Organophosphorus Cationic
Chromophores

2.1. Tailoring terminal phosphonium group to \( \pi \)-conjugated
motifs

The preparation of phosphonium-substituted unsaturated or-
ganic molecules generally relies on the classical methods of
quaternization of tertiary phosphines \( \chi ^{2} \sigma ^{+} \) with alkyl, aryl or
alkyne reagents RX, where X is a halide, sulfonate or azide
(Scheme 1).[7] The arylation protocol conventionally involves Ni-
and Pd-catalyzed P–C bond formation, originally introduced by

![pathway I](source)

pathway I

![pathway II](source)

pathway II

Scheme 1. Common approaches to acyclic phosphonium salts.

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The ORCID identification number(s) for the author(s) of this article can be
found under: https://doi.org/10.1002/chem.202001853.
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The efficiency of this process strongly depends on the stereochemistry and electronic properties of the aryl precursor, as well as the reaction conditions (concentration, solvent, catalyst load), which were later optimized by Charette (routes A and B, Scheme 2), and further adapted for polymer synthesis as well. Despite relatively high temperatures (110–145 °C for Pd and 180–220 °C for Ni-catalyzed P-C coupling), certain functional groups (alcohols, ketones, aldehydes, amides) tolerate this process. A mild approach to quaternary P-arylated compounds is based on photoinduced radical arylation starting from diaryliodonium salts as a radical source in the presence of Ru(bipy)₃Cl₂ as a photoredox catalyst (route C, Scheme 2). Interestingly, the use of sterically hindered unsymmetrical Ar-I⁺-Mes precursors afforded a range of Ar-⁺PPh₃ cations under visible light irradiation (400–410 nm LED) without metal photosensitizer.

A facile metal catalyst-free method to obtain phosphonium salts from oligophenylene and polyaromatic bromides is their coupling with triphenylphosphine in refluxing phenol (e.g. 1a–f, Figure 1), which allows for the utilization of functionalized precursors containing hydroxyl, ether/ester, carboxyl, and N-unsubstituted indolyl groups. A promising regioselective synthesis of 4-pyridine phosphonium derivatives (2a–c, Figure 2) can be carried out under mild conditions by sequential treating the parent pyridine with the triflic anhydride, the phosphine and the base (route E in Diagram).

**Scheme 2.** Metal-catalyzed (A–C) and catalyst-free (D–G) synthetic routes to phosphonium salts (FG = functional group).

**Figure 1.** Examples of π-rich phosphonium salts 1a–f prepared in refluxing phenol (route D).

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**Horner, Heck and Migita.**

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Although these salts have been considered as intermediates to functionalize pyridines in the original publications, the described method can also be a facile way to the novel chromophore phosphonium heterocycles. Alternatively, 2- and 4-halopyridines have been used for the arylation of triphenylphosphine.

Aryl diazonium salts are another type of strong electrophiles, which have been used in the synthesis of dendritic phosphonium cations (Figure 3), where a key step of phosphine quaternization carried out at moderate heating (65 °C) tolerates terminal alkynegroup (route F).

In situ generated arynes (e.g. employing (o-trimethylsilyl)aryl triflates and CsF in acetonitrile) also act as efficient agents to quaternize phosphines (route G). This relatively specific method has been applied to prepare a variety of phosphonium triflates, including those with polyaromatic substituents (e.g. 1b) and P-chiral salts.[21]

Phosphine oxides $\text{R}_3\text{P} = \text{O}$, readily available compounds, when treated with oxalyl chloride (COCl$_2$) are converted into the chlorophosphonium salts [$\text{R}_3\text{PCl}$]Cl, which consequently react with nucleophilic agents, for example, Grignard reagents $\text{RMgX}$, to afford quaternized organic derivatives [$\text{R}_3\text{PR}']\text{Cl}$.[22]

Reactive P–H bonds, for example, in secondary phosphine PPh$_2$H or in protonated tertiary phosphines [$\text{R}_3\text{PH}$]OTf activate 1,2- and 1,4-naphthoquinones, respectively, and afford phosphonium products with dihydroxynaphthyl groups (Scheme 4).[24]

An intriguing case of gold-mediated C–P bond formation has been recently disclosed for C=N cyclometalated complex, which interacts with 1,3,5-triazola-7-phosphaadamantane and reductively eliminates phosphonium salt 6 (Scheme 5).[25] Yet not cost effective, this process might illustrate a key step for the future catalyzed C–P coupling reactions.

In addition to phosphonium salts bearing aryl fragments, alkyne-containing congeners are conveniently formed upon reacting the tertiary phosphine with electrophilic haloalkynes (Scheme 5).

Depending on the reactivity and accessibility of the π-chromophore precursor, the methods belonging to the general pathway I (Scheme 1) might become inefficient, particularly for sterically demanding haloaromatic compounds. As an alterna-

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**Figure 2.** Examples of pyridine phosphonium salts 2a–c.[18]

**Figure 3.** Synthesis of the dendritic phosphonium cations 3.[20]

**Figure 4.** Syntheses of phosphonium salts 7a–c with alkyne π-substituents.[20,21]

**Scheme 2.** Although these salts have been considered as intermediates to functionalize pyridines in the original publications, the described method can also be a facile way to the novel chromophore phosphonium heterocycles. Alternatively, 2- and 4-halopyridines have been used for the arylation of triphenylphosphine.

**Scheme 3.** Aryne insertion into the P=O bond to give aryloxy phosphonium triflates 4.[21,22]

**Scheme 4.** Synthesis of hydroxynaphthyl substituted salts 5a,b.[24]

**Scheme 5.** Gold(III)-mediated synthesis of salt 6 derived from PTA (1,3,5-triazola-7-phosphaadamantane).[21]
tive, such species are first used to obtain tertiary \( \lambda^3 \alpha^3 \) phosphines, which are subsequently quaternized by alkyl halides/triflates (i.e., benzyl, naphthyl, anthyl bromides, and methyl iodide/triflate) under mild conditions (pathway II, Scheme 1). It should be noted that alkyl phosphonium salts suffer from the lack of stability toward bases (i.e., nucleophilic attack), forming phosphorus ylides.\(^{27}\)

2.2. Phosphonium-containing chromophores

2.2.1. Donor–acceptor systems

The pronounced electron withdrawing character of the pendant \( \lambda^3 \sigma^3 \) \( \text{PR}_n \) group makes it an attractive unit to tune the energies of frontier orbitals of the chromophore \( \pi \)-system. In particular, the electron poor nature of \( \lambda^3 \text{PR}_n \) substituents can be used for the construction of donor-acceptor (or push-pull) ionic compounds with large charge separation, which demonstrate distinct photoinduced intramolecular charge transfer (ICT). The electronic properties of the donor (D), acceptor (A) motifs, and the degree of communication between them by means of a \( \pi \)-spacer, control the HOMO-LUMO gap and the ICT, which define the photophysical behavior. In this respect it is essential that the electronic features of the phosphonium motif and the degree of the electron delocalization can be tuned through the modification of \( \pi \)-R groups. Despite the accessible syntheses described above, such \( D-\pi-A^+ \) chromophores are not excessive. The versatile and facile connectivity of the phosphorus atom is also important for the development of multipolar architectures, as it allows for the stepwise synthesis of heterosubstituted compounds of \( [\text{PR}_n]^{-} \) type.

The 3D octupolar chromophores \( 8a/b \) and \( 9 \) (Figure 5) demonstrate non-linear optical (NLO) behavior in solution and crystalline powder, respectively.\(^{28}\) Azo-dyes \( 8 \) were expectedly non-fluorescent. The phosphorus connecting center brings together several virtually non-interacting chromophore arms that additively increased hyperpolarizability of \( 8a \) and \( 8b \) compared to their dipolar relative \( 8c \). According to quantum chemical calculations, the phosphonium group \( \lambda^3 \text{PPh}_3 \)Me of \( 8c \) does not serve as a true electron acceptor. Instead, it strongly polarizes the adjacent phenylene ring and therefore stabilizes the negative charge transfer from the electron rich amino-phenylene part upon photoexcitation. This ICT results in the inversion of the direction of the dipole moment in the excited state, which is destabilized in more polar solvents leading to the negative solvatochromism (e.g., \( \lambda_{\text{abs}} \) for \( 8a \) shift from 511 nm in CHCl\(_3\) to 499 nm in MeCN). The symmetrical anisole-derived salt \( 9 \) was shown to produce moderate second-harmonic generation and thus illustrates a way to NLO materials by means of crystal engineering of simple ionic compounds.

The zwitterionic betaine dyes \( 10 \)\(^{29a,29d} \) and \( 11 \)\(^{29c} \) (Figure 6) reveal more drastic absorption changes in different solvents than \( 8 \). Thus, \( 10 \) \( (R = R' = \text{Ph}) \) is red in methanol \( \lambda_{\text{abs}} = 498 \text{ nm} \), purple in dichloromethane \( \lambda_{\text{abs}} = 596 \text{ nm} \) and green in toluene \( \lambda_{\text{abs}} = 686 \text{ nm} \), giving a hypsochromic shift of the lowest energy (charge transfer) absorption band of \( = 5500 \text{ cm}^{-1} \) (\( = 188 \text{ nm} \)). The substituents at the phosphorus atom in \( 10 \) have a distinct influence on the absorption maxima, which appear at 20–30 nm longer wavelengths for \( R = \text{Ph} \) vs. \( R = \text{Bu} \). The alteration of \( R' \) groups (Ph→Bu) shows an opposite effect of approximately the same magnitude; however, the largest hypsochromic shift (ca. 90 nm) of the absorption within this family was achieved when the butyl motif was replaced by the more polar chloride at the \( R' \) positions. Unfortunately, no information was provided concerning the emission properties of compounds \( 10 \) and \( 11 \).

The negative solvatochromic behavior of cationic donor-acceptor salts \( 12 \) \( (\lambda_{\text{abs}} = 422 \text{ nm in MeOH and } 442 \text{ nm dichloromethane for } n = 2) \) is quite moderate compared to that of betaines \( 10 \) and \( 11 \)\(^{29c} \) which can be attributed to a less polar ground state of the ionic dyes. Compounds \( 12 \) were reported to be fluorescent in solution and are evidently prone to photoinduced ICT leading to an appreciable charge redistribution (Figure 6), which in turn might affect the anion-cation interaction (see section 4 below).

The modulation of the ICT in simple phosphonium salts \( 13, 14 \) containing chemically active aryborane functions suits for highly sensitive fluorescent and colorimetric detection of the fluoride anion (Figure 7).\(^{30} \) The zwitterionic character of the phosphonium group allows to perform the analysis in aqueous medium. Importantly, the Lewis acidity of the borane unit is readily regulated by the substituents at the \( P \) atom and reaches its maximum for compound \( 13d \) \( (R = \text{Ph}) \), which shows the highest affinity for the fluoride. This efficient complexation of the \( F^- \) by the borane combined with cell penetrating ability of

![Figure 5. NLO-active branched octupolar donor-acceptor cations 8a,b, 9 and the dipolar congener 8c.](image)

![Figure 6. Negatively solvatochromic phosphonium betaine dyes 10, 11 and the dipolar donor-acceptor salts 12; the proposed photoinduced transitions to less polar states for 10 and 12 are shown.](image)
the phosphonium group has been lately applied for the selective transport of this anion across phospholipid membrane by 13b and similar compounds. Another way to enhance both the acidity of the boron atom and the electrostatic effect for anion sensing is exemplified by the arylboranes (Mes)_3B(ArP^+)(ArP^+) (Mes = 4-(MePh_2P^+)-2,6-Me_2C_6H_2) bearing one (15a, x = 1), two (15b, x = 2) and three (15c, x = 3, Figure 7) phosphonium substituents. Among these species, the tricationic borane 15b is capable of most efficient binding cyanide ions in water at pH of 7 (K = 1.7 x 10^10 M^-1), accompanied by clearly detectable changes in the absorption spectra. Noteworthy, in borane-phosphonium compounds, the -BMes_2 group, despite being an electron deficient motif, can be the main contributor to HOMO according to the DFT analysis, and therefore during the photoinduced charge transfer is considered as a weak donor with respect to the cationic highly polarizing -PR_3 fragment. The electron richer 1,3,2-benzodiazaborole function leads to a more distinct push-pull character of salts 16 (Figure 8), which reveals visibly smaller HOMO-LUMO gaps (predicted 3.075–3.099 eV) in comparison to its phosphate-chalcogenide relatives (predicted 4.093–4.394 eV) due to the lower lying LUMO levels.

The decrease of the optical gap does not necessarily require donor-acceptor architecture and can be achieved by decorating the π-system with terminal phosphonium groups; for example, the emission maxima for compounds 17a–c are bathochromically shifted relatively to their non-substituted analogues for 33–65 nm (894–3338 cm^-1). This strategy has been successfully employed in the fabrication of phosphonium-linked fluorescent polyelectrolytes. Nevertheless, the combination of the phosphonium group with a strong electron donor gives D-π-A+ dyes with wide tunability of the optical band gap (compounds 18, Figure 8). For example, the oligophenylene-based salts 18a–d are brightly fluorescent in dichloromethane solutions (\( \Phi_{em} = 0.71–0.95 \)) with emission wavelength changing from blue (487 nm) to orange (619 nm) upon increasing the number of the phenylene rings in the π-spacer. Remarkably, the pyridinium donor–acceptor dyes, including the direct congeners of the phosphonium salts 18a–c, exhibit much lower quantum efficiencies (typically less than 0.01). The use of the polyaromatic (acene) π-system ultimately results in deep-red luminescence (\( \lambda_{em} = 696 \) nm for 18g in dichloromethane), though with a much lower quantum yield of 0.02 only. These compounds demonstrate good two-photon absorption (TPA) cross-section up to 321 GM (Goeppert-Mayer GM = 1 x 10^{-44} cm^4/s photon^2 molecule^-1) for phenylene series (18d), while derivative 18f reaches the value of 977 GM at the excitation of 800 nm.

2.2.2. Phosphonium-modified dyes

Appending terminal phosphonium motifs to hydrophobic organic dyes is a suitable method to increase their biocompatibility. It has been actively used for the development of various

![Figure 7. Complexation of the fluoride and cyanide ions with phosphonium boranes 13[30a,b, 14[30c] and 15[30d] (inset photographs show the corresponding fluorescence responses). Adapted from reference [30a] with permission from The Royal Society of Chemistry (2020). Adapted from reference [30c] with permission from American Chemical Society (2020).](image)

![Figure 8. Schematic structures of the D-π-A+ (16, 18)[30c, 36] and A+ -π-A+ (17)[36] linear λ,σ* phosphonium chromophores (the photo shows dichloromethane solutions of 18a-d under UV light). Adapted from reference [36] with the permission of Wiley-VCH GmbH (2020).](image)
probes to target mitochondria, although in most of the cases the P-cationic group is electronically innocent as it is isolated from the chromophore scaffold by an aliphatic spacer.\(^{[10]}\) The examples of a direct bonding of the phosphonium fragment to the dye molecules are rare, which, for instance, comprise coumarin and BODIPY derivatives \(19^{[38]}\) and \(20^{[39]}\) (Figure 9), showing specific mitochondrion localization. The quantum yield of \(19\) reaches 0.91 in dichloromethane \((\lambda_{\text{em}} = 441\) nm\)), whereas for unsubstituted 7-methoxycoumarin the emission intensity is lower \((\Phi = 0.53\) in buffer and 0.03 in methanol\)) and the energy is substantially higher \((\lambda_{\text{em}} = 394\) nm\)),\(^{[40]}\) indicating a non-innocent effect of \(\text{PMEtol}^+\) electron acceptor on the photophysics of the parent dye.

The reversible formation of the phosphonium adducts as a result of nucleophilic addition of phosphines to cyanine or squaraine dyes offers unconventional stimuli-responsive systems.\(^{[41]}\) For instance, the equilibrium between intensely blue colored squaraine and the bleached adduct is regulated by nucleophilicity of the \(\text{PR}_3^+\) reagent as well as temperature (Figure 10). The adducts \(21\) also have a potential to serve as chemodosimeters for the metal ions and complexes that have high affinity to phosphine ligands (e.g. Rh, Pd, Ir, Au).\(^{[41c]}\)

Decoration of the naphthalenediimide with phosphonium groups generates stable ultra-electron deficient species \(22\) (Figure 11A) having exceptionally low LUMO energy of \(-4.90\) eV and the first reduction peak at \(-0.199\) V (vs. Fc\(^+/\)Fc).\(^{[42]}\) The corresponding radical ion \(22\)b, which can be efficiently prepared from the diimide dibromide and the phosphine under solvent-free conditions,\(^{[43]}\) appears to be highly stable and tolerates conventional workup operations on air. This feature arises to a large extent from hypervalent Lewis acid-base \((\text{P}^+\cdot\text{O})\) interactions, which are known for other phosphonium salts with hard donors.\(^{[44]}\) An easy electron transfer to \(22\)a that is accompanied by a dramatic color change (Figure 11B), and extraordinary stability of radical \(22\)b form an attractive platform for switchable electrochromic materials. Moreover, the judicious choice of the \(R\) and \(R'\) groups made possible the isolation of highly electron rich doubly reduced derivatives \(22\)c with diverse color palette.\(^{[45]}\)

Two step reversible reduction with waves at \(-0.28\) and \(-0.90\) V (vs. Fc\(^+/\)Fc) has been also realized in the \(\alpha\)-phosphonio-acridinium dication \(23\)a that produced air-stable phosphonio-radical, and ultimately an easy to decompose antiaromatic phosphorus ylide \(23\)c (Figure 11A).\(^{[46]}\) On the other side, the use of pyromellitic diimide motif allows to obtain highly stable...
chromophoric ylide 24, which does not show typical Wittig reactivity. Its persistence has been attributed to O:C:P interactions indicated by the natural bond orbital calculations.

3. Cyclic Organophosphorus Cationic Chromophores

3.1. Synthetic approaches to ionic phospha-annulated systems

The methods of merging the phosphonium function \( R^3 P^+ < \) into the \( \pi \)-conjugated scaffold yet have not been a subject of systematic studies, and therefore the number of general protocols are still quite limited. The reported approaches can be roughly classified into three main categories depicted in Scheme 6.

3.1.1. Quaternization of \( \lambda^3 \sigma^2 \) P-heterocycles

Arguably the most straightforward way to obtain ionic phosphacyclic chromophores is based on the preparation of parent \( \lambda^3 \sigma^2 \)-P cyclic chromophores and their subsequent \( \lambda^3 \sigma^2 \) quaternization (pathway I, Scheme 6), which has been exploited for a wide selection of alkylation agents RX having different leaving groups (X = halides, mesylate, tosylate, or triflate).

Ring-fused phosphole systems serve as a source for phospholium acenes (Figure 12).46 The six-membered organophosphorus cations also can be prepared by alkylation of cyclic \( \lambda^3 \sigma^2 \)-predecessors.46

In comparison to the tertiary phosphines, lower nucleophilicity of the \( \lambda^3 \sigma^2 \) P atom in phospholes evidently makes it less reactive toward arylation; so far there has been only one example of direct Pd-catalyzed P-arylation of the benzo[b]phosphole.46

3.1.2. Intramolecular phosphacyclization

Fusing phosphacyclic ionic scaffolds with conjugated hydrocarbon systems can be achieved by means of various intramolecular reactions, which imply the incorporation of P–C bond formation (pathway II, Scheme 6). Following this methodology, the preparation of arylyphospholium salts often involves activation of the alkyne motif that is in ortho-position to the phosphorus center (Scheme 7).

An efficient metal-free synthesis to phospholium-borate zwitterionic ladder stilbenes 25 was disclosed by Yamaguchi group (route A).50 The electron-donating substituents at the phosphorus atoms (R = tBu and Cy) result in immediate nucleophilic cascade cyclization of the intermediate phosphine at room temperature, whereas for R = Ph thermal or photochemical initiation is required.51

The closure of 5-membered phospha-ring occurs in the course of phosphinoarylation of alkynes (route B, Scheme 7), the gold center can be subsequently removed with strong acid to afford cations of a family 26.52 This sort of reaction can be carried out without metal reagent as it is promoted by excess of protic acid.53 The dialkynyl precursors of suitable stereochemistry undergo cascade process, where the first step of stoichiometric phosphinoarylation is followed by a gold-catalyzed cyclization to afford fused \( \pi \)-extended salts 27 in up to quantitative yields (Scheme 8).54

Importantly, readily obtainable phosphine oxides can also be transformed into phospholium derivatives in good yields. Their treatment with oxalyl chloride gives electrophilic \( \lambda^5 \sigma^5 \)-chlorophosphonium intermediates, which then transform into the heterocycle at moderately elevated temperature (70 °C, route C, Scheme 7).55

**Scheme 6.** General routes to embed P-quaternized group into aromatic cyclic scaffold.

**Scheme 7.** Examples of intramolecular alkyne cyclization reactions to produce phospholium compounds.

**Scheme 8.** Domino synthesis of fused phospholium derivatives 27.54
Copper(II)-mediated intramolecular phosphacyclization, based on C–H activation with phosphoniumyl radical formed via single electron transfer, appeared to be a convenient protocol to convert ortho-functionalized tertiary phosphines into five- and particularly six-membered cationic heterocycles (Scheme 9).

The method was first demonstrated for the BINAP diphosphine (2,2′-bis(diphenylphosphino)-1,1′-binaphthyl), which delivered diphosphonium salt 28 in moderate 24% yield when reacted with 1 equiv. of Cu(OTf)₂. This strategy was later applied under optimized conditions to a variety of polyaromatic hydrocarbon backbones, affording a series of PAH-phosphacyclic species 29 (Scheme 9). Altering the nature of the ortho-substituent, a similar reaction as well can be employed for the synthesis of phospholium cations 30.

It was also noted that stoichiometric amount of PhICl₂ can oxidize 1,3,5-tris(diphenylphosphino)benzene into a reactive intermediate, which quantitatively cyclizes into phosphaphenalene cation 31 (Scheme 10); however this method was inefficient for the preparation of 29-type salts.

### 3.1.3. Intermolecular phosphacyclization

The intermolecular condensation/cycloaddition reactions leading to the formation of phospha-rings recently have received considerable attention. An elegant single-step procedure has been pioneered by Wang and co-authors, who applied a copper(II)-mediated cycloaddition of alkynes to tertiary phosphines, yielding five- (32) or six-membered (33) P-heterocyclic cations in high yields (Scheme 11 A).

In yet another approach, benzynes undergo insertion into the P=N bond of P-alkenyl/alkynyl-λ⁴-phosphazenes. The subsequent cascade intramolecular transformations deliver 1,4-benzophosphorinium cations 34, which offer promising possibilities for functionalization and tuning the electronic properties (Scheme 11 B and C).

3.2. Tuning optical properties of ionic phospha-annulated chromophores

#### 3.2.1. Phospholium-based dyes

Photophysical behavior of P-heterocyclic dyes has been predominantly investigated for the systems containing 5-membered rings, along with a growing number of the reports on the 6-membered congeners. The electron-accepting properties of λ⁴(π) and λ⁴(π)-phosphate derivatives, assigned to the low energy of the LUMO, have been explained by the phenomen-
The electrophilicity of phosphole-containing species evidently depends on the substituents on the phosphorus atom, and is particularly enhanced for $\lambda'\alpha'$ cationic compounds.\cite{8a} The incorporation of strongly electron deficient P-ionic motif into the $\pi$-conjugated scaffold dramatically affects frontier molecular orbitals of the latter. Clearly, the optoelectronic characteristics of such phospha-annulated systems are primarily dictated by the structure and the composition of the organic framework, but they also can be modulated by means of the ancillary substituents at the phosphorus atom and the counterion component.

One of the simplest motifs used for the construction of phosphacenic chromophores is benzophospholium unit (Figure 13). The resulting phenyl-substituted salts 26a-c with moderate ICT are intense blue emitters in solution ($\lambda_{em}=446$ nm $R=H$, 476 nm $R=OMe, CH_2Cl_2$) with quantum yields ranging from 0.75 to 0.89 for PF$_6^-$ or OTf$^-$ anions.\cite{8a,5} In the case of iodide, the intensity of fluorescence is systematically lower ($\Phi_{em}=0.36-0.80$) that might be a result of anion-$\pi$ charge transfer interaction.\cite{5} The bulkier groups at the phosphorus atom lead to a certain improvement of quantum efficiency by suppressing non-radiative decay rate; for example, the methylated derivative 26a shows twice larger $k_{nr}$ ($3 \times 10^7$ s$^{-1}$) than ethylated and phenylanged congeners 26b,c ($k_{nr}=1.4 \times 10^7$ s$^{-1}$).\cite{5}

The decrease of the optical gap has been also realized in phosphofluorolanes 37 and 38 by decorating the dibenzo-phospholium motif with diethylamino styryl donors.\cite{9a} Salt 38, a rare example of spiro- phosphonium compounds, shows deep-red to near-IR fluorescence with $\lambda_{em}=695$ nm ($\Phi_{em}=0.1$) in toluene and 715 nm in CH$_2Cl_2$ ($\Phi_{em}=0.04$). The essential impact of the spiro-structure is reflected not only by the red shift of the absorption and emission bands, but also by almost 3-fold increase of the TPA cross-section, which amounts to 1022 GM (at 932 nm) for 38 and 356 GM for 37.

Modification of the phenyl-benzophospholium 26a with the secondary heteroatom (sulfur) virtually does not change the fluorescence wavelength (39a: $\lambda_{em}=445$ nm, $\Phi_{em}=0.36$ in CH$_2Cl_2$).\cite{9a} The electronic state of sulfur however affects the conjugation within the heterocyclic core, and the electronic behavior of the phosphorus. Oxidation of the S-atom converts it into an electron accepting group (39b), diminishes the band gap and drastically suppresses the non-radiative relaxation of the excited state ($k_{nr}=4.3 \times 10^7$ s$^{-1}$ for 39a and 0.1 $\times 10^7$ s$^{-1}$ for 39b), giving the quantum efficiency close to unity (39b: $\lambda_{em}=483$ nm, $\Phi_{em}=0.99$ in CH$_2Cl_2$). Several other thienophospholium derivatives, as well studied by the group of Baumgarten,\cite{9b,6} were elegantly engineered via the modification of both the conjugated backbone and the auxiliary substituents at the phosphorus atom. These chromophores demonstrate intriguing stimuli-responsive fluorochromism and aggregation-induced emission (AIE), which have been discussed earlier.

The symmetrical dicaticonic stilbenes 40a,b (Figure 13) are brightly fluorescent in both solution and solid state.\cite{9b} Remarkably, chloride 40b gives the quantum yield of 0.74 in water ($\lambda_{em}=518$ nm) with significant Stokes shift of 5780 cm$^{-1}$ that makes this motif an attractive paradigm for bioimaging purposes. On the other hand, relatively low-lying LUMOs (CV$_{LUMO}=-4.19$ and $-4.04$ eV for 40a,b) favor electron injection, suggesting that these electron-accepting species can be employed for the development of n-type semiconducting materials.

High electron affinity has been also demonstrated by the dyes with extended polyaromatic system. Dianacenaphthophospholium salt 41 (Figure 14) shows low reduction potential of only $-1.00$ V (vs. Fc$^-$/Fc), which is less negative than that of congener neutral phosphates apparently due to the electron deficient nature of the P-cationic center.\cite{9b}

Photoluminescent properties of the phosphacenes are distinctly dictated by the size and stereochemistry of the p-backbone. If 41 is a weakly deep-red fluorophore ($\lambda_{em}=684$ nm, $\Phi_{em}<0.01$ in CH$_2Cl_2$), the binaphthyl derivative 42 has been described as bright green-yellow emitter in crystalline state.\cite{10a}

Planarized PAH framework in dibenzophosphapentaphenes 43 provided highly delocalized p MO-s (Figure 14).\cite{10a} The cationic character of 43a,b is manifested by the significant contribution of the P atom to the LUMO and higher reduction potential vs. their chalcogenide analogues. The methylated derivative 43a reveals moderately intense orange-red fluorescence ($\lambda_{em}=599$ nm, $\Phi_{em}=0.19$ in CH$_2Cl_2$). Importantly, air- and moisture-stable thio-phospholium compound 43b, which was obtained by treating the corresponding sulfide with MeOTf, shows spectacular bathochromic shifts of both the lowest

![Figure 13](image13.png)

![Figure 14](image14.png)
energy absorption (from 554 to ca. 610 nm) and emission (to 669 nm) bands compared to 43a. Considering the enhanced electron-accepting ability of R3P+-SCMe motif, its stability and the easiness of preparation, 43b illustrates a very attractive yet undeveloped way to decrease optical band gap of donor-acceptor organophosphorus chromophores.

ICT has been successfully tuned in zwitterionic stilbenes 25 (Scheme 7) and their extended polycyclic derivatives that allowed to vary the emission from green to red-orange ($\lambda_{em} = 517–623$ nm in tetrahydrofuran)\(^{[50, 51]}\). The concept of embedding cationic phospholium (acceptor) and anionic borate (donor) units in the same molecular scaffold was further accomplished in 44, which was readily obtained from the ortho-alkynyl triphenyl phosphine and B(C$_6$F$_5$)$_3$ as an electrophile in a nearly quantitative yield (Figure 15).\(^{[53]}\)

The presence of the borate substituent in 44 has a minor influence on the emission parameters ($\lambda_{em} = 471$ nm, $\phi_{em} = 0.76$ in CH$_2$Cl$_2$) with respect to its predecessor 26b ($\lambda_{em} = 476$ nm, $\phi_{em} = 0.88$), but considerably increases the Stokes shift from 4633 cm$^{-1}$ (26b) to 8709 cm$^{-1}$ (44).

The series of zwitterionic carbones 45 are also bright blue emitters ($\lambda_{em} = 446–469$ nm, $\phi_{em} = 0.34–0.99$ in CH$_2$Cl$_2$).\(^{[21]}\) In contrast to the donor-functionalized 26d with red fluorescence,\(^{[48]}\) compound 45 with the same diphenyl-aniline substituent does not exhibit low energy ICT due to the localization of the HOMO on the carborane fragment. The peculiar feature of compounds 45 lies in their remarkable easiness of the reduction, which occurs at the potential $E_{1/2}$ ranging from $-1.02$ to just $-0.4$ V (vs. Fc$^-$/Fc) according to electrochemical data.

### 3.2.2. Chromophores containing six-membered P-cationic heterocycles

The development of photofunctional molecular materials based on six-membered P-heterocycles has been considerably delayed in comparison to the corresponding phosphole chemistry.\(^{[64]}\) Nevertheless, such phospha-annelated systems apparently offer rich opportunities for ring modification, and can introduce new chemical and electronic properties, which might be difficult to attain with other cyclic motifs. The so far very limited examples of compounds, incorporating six-membered P-cationic rings, are classified as $\lambda^1\sigma^2$-endo, $\sigma^2$-exo species. Their optical behavior is determined by the $\pi$-conjugated backbone, akin to phosphole derivatives. The fluorescence has been detected for compounds with acene backbones, while very weak or no emission was reported for structurally simpler cations (e.g. dibenzophosphoniodine,\(^{[50a, 71]}\) dithienodihydrophosphonine,\(^{[49a]}\) acidophosphine\(^{[46]}\) derivatives).

For thiaphosphinine 46 composed of two benzothienyl units (Figure 16), the dynamic luminescence has been observed; the high energy emission band ($\lambda_{em} = 387$ nm) transforms into bathochromically shifted band ($\lambda_{em} = 513$ nm, $\phi_{em} = 0.02$) as the concentration increases.\(^{[71]}\) This behavior was assigned to an excimer formation, rather unusual for ionic dyes, which also explains solid state fluorescence ($\lambda_{em} = 535$ nm).

The naphthalene-based fluorophores 29a, 47 and 48a–g (Figure 16) reveal strong impact of non-acene fragment of the backbone on the photophysical performance. Relatively weak deep blue emission of thienyl compound 47 ($\lambda_{em} = 418$ nm, $\phi_{em} = 0.07$ in CH$_2$Cl$_2$)\(^{[49b]}\) is significantly improved in its phenylene congener 29a ($\lambda_{em} = 418$ nm, $\phi_{em} = 0.3$ in CH$_2$Cl$_2$).\(^{[57b]}\) Salts 48, obtained via alkyne insertion into phospharuthenacycles followed by P-C reductive elimination, are luminescent for aromatic R substituents only.\(^{[24]}\) The emission is tuned from $\lambda_{em} = 531$ (48e, $\phi_{em} = 0.03$ in CH$_2$Cl$_2$) to 588 nm (48g, $\phi_{em} = 0.46$) primarily by changing the energy of the HOMO, to which the pendant aryl R groups make the dominant contribution, whereas the LUMO localized on the phosphophenalenium core remains rather unaffected. The modulation of the emission wavelength by moving from R=Ph (48c) to p-C$_6$H$_4$OMe (48g,}
Δλ = 54 nm, 1720 cm⁻¹) is considerably more efficient than that for the analogous structural variation of the abovementioned phospholium dyes 26b and 26c (Δλ = 23 nm, 1067 cm⁻¹). It is worth noting that compounds 48c–g are intensely fluorescent in the solid with quantum yields up to 0.77 (48g) and hypsochromic shift of the emission maxima (λem = 422–507 nm). These features are attributed to the absence of π-stacking interactions prevented by the bulky counterion BA 4%.

The employment of different acene cores together with donor-acceptor architecture in 29a–h allows to alter the fluorescence through the entire visible range (λem = 418–780 nm in CH2Cl2, Figure 16B) with good quantum yield even in the near-IR region (29h, λem = 780 nm, Φem = 0.18 in CH2Cl2).57 Due to the ionic nature, most of salts 29a–i are moderately soluble in water. Importantly, some of these species retain intense emission in aqueous medium (Φem = 1 for 29c–e in H2O) and demonstrate good TPA properties (the corresponding cross-section for 29c–f ranges from 310 to 637 GM measured at 800 nm in water).58 It has been shown that these photophysical properties, together with high photostability and low toxicity, make anthracene-based dyes 29c–h applicable in one- and two-photon cell imaging.

The involvement of the quaternized cycle-embedded phosphorus atom into the LUMO means that increasing the number of the cationic centers connected via π-conjugated skeleton necessarily influences frontier orbitals, optical band gap and the electrochemical properties of the system. In line with dicaticonic nature, the diphosphahexaarene 49 (Figure 17) presents a set of reduction potentials with the lowest value of −1.1 V, while no oxidation was observed.59 This points to high stability of the cation, also confirmed by the absence of photodegradation under prolonged irradiation. The vibronic-structured emission of 49 in solution (λem = 422 nm, Φem = 0.8 in CH2Cl2) remains nearly the same in water (λem = 423 nm, Φem = 0.67) providing the opportunities for biovisualization.

An interesting set of dicaticonic molecules (selected examples 50–52 are given in Figure 17) has been recently described by Bouit and co-workers, prepared from tertiary diphosphines and diphenylacetylene (method A, Scheme 11).53,56 Decoration of the naphthalene with phosphininium rings produces 1,8-bisphosphapryrenium 50 scaffold with orange fluorescence (λem = 606 nm, Φem = 0.19 in CH2Cl2). Similarly, the binaphthyl dication 2886 reveals further blue shift and emits comparably to 49 (λem = 453 nm, Φem = 0.11 in water).67 On the downside, 52 possessing anthracene motif shows deep-red fluorescence (λem = 672 nm, Φem = 0.04 in CH2Cl2) even without involving strong donor groups, which confirms the importance of P³⁺-PAH connectivity but not only the size of the aromatic framework. It is essential that salts 50–52 are also bright emitters in solid (Φem = 0.11–0.39) including 52, the fluorescence of which is almost unaltered (λem = 670 nm). Along with the optical data, 52 is the easiest ion to reduce in this series (Ered = −0.64 V vs. Fc⁻/Fc), all dications displaying two separated “viologen-like” reduction waves in accordance with their structures.

4. Cation–Anion Interactions in P-Cationic Chromophores

The electrostatic noncovalent interactions between the charged components are known to have a substantial effect on the photophysical properties of the ionic dyes.60–64 Thus, it has been shown that the intensity of the pyridinium–π exciplex emission depends on the nature of the counterion, and is enhanced in the presence of PF₆⁻ but quenched with halides.65 The related phenomena of anion-responsive absorption and/or emission behavior have been also encountered for the P-cationic chromophores. Thus, the fluorescence of the dicaticionic compound 17b in moderately polar dichloromethane can be regulated by the anion and the concentration (Scheme 12).34c At high concentration (which corresponds to the optical density (O.D.) of 1.0) the iodide salt of 17b is weakly emissive (Φem = 0.07), and the fitting of the decay curves gives three different lifetimes (τ varies from 0.04 to 2.7 ns). In dilute solution (O.D. = 0.1) the quantum yield increases to 0.24, whereas the change of the anion (for PF₆⁻) or the solvent (e.g., methanol) leads to a single exponential decay (τ = 2.8 ns) and more dra-

Figure 17. Fluorescent dicaticonic six-membered phosphacycles fused with acene motifs.34c,64

Scheme 12. Proposed equilibrium for salts 17b and 26a,b in solution.34c,64
matic improvement of the luminescence efficiency to 0.86 and 0.77, respectively, at the O.D. of 1.0. These observations were rationalized by the equilibrium between the contact and solvent separated ion pairs. As proposed by the authors, the non-dissociated state is favored by the iodide and higher concentration in the less polar medium (CH$_2$Cl$_2$), resulting in (i) the presence of several emissive species, and (ii) quenching of luminescence due to the heavy atom effect. The same group further extended the concept of ion pairs on phosphonium fluorophores 26a,b (Scheme 12). These species also reveal a systematic increase of the emission intensity in lower polarity solvent for the hexafluorophosphates compared to the iodide analogues, mainly due to the suppression of non-radiative decay rate.$^{[46a]}$ Although anions have a significant impact on the efficiency of fluorescence for contact ion pairs, the energies of the radiative transitions remain virtually unchanged. In stark contrast, the linear D-$\pi$-A$^+$ oligophenylene salts 18a-c (Figure 8) feature unconventional dual emission in non-polar solvents (toluene, dioxane, carbon tetrachloride).$^{[46b]}$ The ratio of two energetically distinct emission bands (e.g. $\lambda_{em} = 468$ and 592 nm for 18b in toluene, $\Phi_{em} = 0.17$), which appear as a result of a continuous spectral temporal evolution (Figure 18), strongly depends on the nature of the counteranion, the length of the $\pi$-spacer, solvent viscosity and the temperature. Such relaxation dynamics has been attributed to the hypothesized anion migration that occurs in donor-acceptor contact ion pairs upon photoinduced ICT in the absence of solvent relaxation (Figure 18C), and ultimately produces a lower energy emissive excited state. It should be mentioned, in support of the mechanism, that the anion migration in the excited ion pair has been also proposed for some N-heterocyclic (acidinium, napthoquinolinium) cationic dyes.$^{[46a,d,75]}$

No less important can be the role of the counterion in the solid-state emission of P-cationic luminophores. It has been noticed for liquid crystalline thienyl phosphonium fluorophores that intermolecular arrangement and, as a consequence, the photophysical properties of the bulk material, can be adjusted by steric and electronic effects imposed by counterions.$^{[46a]}$ Hence, in the studied series (Br$^-$, BF$_4^-$, BPh$_4^-$, OTf$^-$) the anions of larger size diminish the probability of $\pi$-stacking that decreases the difference between the solution and solid state emission, and might increase the quantum yield. Moreover, the substitution of small bromide for amphiphilic dodecylsulfate combined with cationic lipid 53 clearly decreases the crystallinity of the solid and limits the AIE property (Figure 19), highlighting an opportunity to control the morphology and optical characteristics of the ionic material.$^{[76]}$

On the other hand, the anions prone to form strong non-covalent interactions are capable to facilitate AIE behavior. AIE-active phosphonium 54 crystallized with polyoxometalates $[\text{M}_6\text{O}_{19}\text{W}]^{12−}$ (M = Mo, W), shown in Figure 20, are involved in the extensive network of anion-$\pi$ interactions and C–H–O hydrogen bonding, while the $\pi$–$\pi$ stacking is prevented upon incorporating the bulky anions as spacers. These multiple contacts rigidify the fluorescent cation that raises the quantum yield almost 3-fold ($\Phi_{em} = 0.43$) with respect to its triflate salt ($\Phi_{em} = 0.15$) and ca. 90-fold compared to that in the solution.$^{[77]}$

Although phosphonium groups in salts 55 and 56 are separated from the polyaromatic $\pi$-systems by the methylene...
In particular, variation of counterions from Br
Eur. Polym. J. 2019
Theor. Exp. Chem. 2016
55
55
56
55
56
X = Br
X = NTf
λ_em = 525 nm
λ_em = ca. 560 nm
grinding
grinding

Figure 21. Phosphonium salts 55 and 56 containing polyaromatic chromophores (photos show the effect of grinding for 55 (left), and of the counter-ion on the solid state emission of 56 (right).) Adapted from reference [78] with permission from The Royal Society of Chemistry (2020).

The anion-cation interactions (anion = Cl-, Br-, I-, NO3-, BF4-, PF6-, BPh4-) involving phosphonio-diimide radical ions of the type 22b (Figure 11A) as well have shown an ability to amend the photophysical and magnetic properties of the cationic π-radical systems. In crystals, the radical cations form various supramolecular assemblies utilizing charge-assisted hydrogen bonding and anion-π contacts. Ion pairing effect appears to be non-innocent in solution too, especially in the solvent of lower polarity. For example, the UV-vis measurements supported by theoretical calculations suggest that nitrate radical salts undergo unusual “reverse” π—anion photoinduced electron transfer in contrast to other anions.[90]

5. Concluding Remarks

In this minireview we tried to highlight the reported data on the organophosphorus ionic chromophores, in which the P-cationic groups play an active role in composing the electronic structures, and therefore show a clear influence on the optical and/or electrochemical properties. These dyes still can be considered as an emerging class of compounds as most of the relevant works have been published during the last decade. The diverse synthetic pathways to π-conjugated P-cations, particularly to P-heterocyclic species, go far beyond simple quaternization of λπππ tertiary phosphines, and can produce intriguing molecular scaffolds, many of which very probably are still undiscovered. Strong electron deficient character of λπππ (and λπσ) phosphorus centers, which can be tuned with the help of the substituents, is immensely useful in the construction of fascinating donor-acceptor systems exhibiting versatile charge transfer and redox behavior. In addition, the unique connectivity of the pyramidal phosphorus atom allows the design and accessible preparation of branched multipolar and multichromophore architectures, although this option has been exploited yet to a very limited extent. Taking into account the charged nature of the described chromophores, the effect of cation-anion interactions and ion pair formation both in the solid and in solution cannot be neglected. Albeit ion pairing brings an additional degree of freedom, which is often difficult to evaluate precisely and to control in reproducible and predictable manner, simultaneously it can greatly diversify physical and chemical properties of two-component aggregates, leading to unconventional phenomena and functionalities that may be far-reaching in both fundamental and applications.

Acknowledgements

A.B. and I.O.K. thank Academy of Finland (grant 317993), and Flagship Programme, Photonics Research and Innovation PREIN, decision 320166). P.-T.C. thanks Ministry of Science and Technology of Taiwan (MOST 109-2923-M-002-003).

Conflict of interest

The authors declare no conflict of interest.

Keywords: anion–cation interactions · ionic dyes · organophosphorus chromophores · phosphonium salts · phosphorus heterocycles

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Manuscript received: April 16, 2020
Accepted manuscript online: June 3, 2020
Version of record online: October 30, 2020