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Phospha-cyanines in their Ideal Polymethine State: Synthesis and Structure-Properties Relationships

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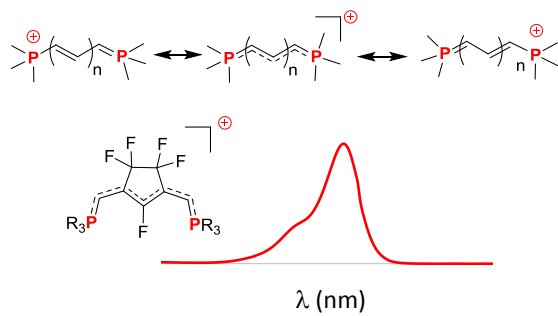
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ABSTRACT. We report the synthesis and full characterization of a family of phosphorus containing polymethine cyanines (phospha-cyanines). The compounds are easily prepared in two steps starting from readily available phosphanes. The impact of the P-substituents and the counterions on the structural and optical properties is investigated through a joint experimental/theoretical approach. Based on the study of the single crystal X-ray diffraction structures, all phospha-cyanines present a bond length alternation (BLA) close to zero, independently of the substituent and the counterions, which indicates an ideal polymethine state. All these compounds display the typical cyanine-like UV-vis absorption with an intense and sharp transition with a vibronic shoulder, despite possessing a reverse electronic configuration compared to “classical” cyanines. TD-DFT calculations allowed to fully rationalize the optical properties (absorption/emission wavelengths, luminescence quantum yields). Interestingly, due to the tetrahedral shape of the P-atom, the optical properties are independent of the counterion, which is in marked contrast with N-analogs, which enables predictive engineering of the phospha-cyanines regardless of the medium in which they are used.

TOC GRAPHICS



KEYWORDS. Chromophore, Pentamethine, π -delocalization, Optical properties, TD-DFT.

Introduction.

Polymethine cyanines are organic compounds in which a charge (either positive such **A**, Fig 1, or negative) is fully delocalized between two heteroatoms (or heterocycles) over an odd number of sp^2 carbon atoms.^{1,2,3} This particular structure, called the ideal polymethine state (IPS) leads to a series of hallmark properties: (i) a bond length alternation (BLA) equal to zero as all the C-C bonds display a “one and a half” bond length, (ii) a sharp and particularly intense absorption band with a vibronic shoulder at high energy, and (iii) luminescence with a very small Stokes shift. The molecular engineering of the structure (polymethine chain length, nature of the heterocycle, counter-ion, central substituent) allowed to tune the absorption/emission of these dyes from the visible to the near infrared.^{4,5,6,7,8,9} Polymethine cyanines thus represent a fascinating platform to study the effect of the molecular structures on electronic delocalization as their exceptional characteristics can vanish when the “cyanine limit” is crossed.¹⁰ Thanks to these hallmark properties, cyanine dyes have been used in many applications in chemical detection,¹¹ bio-imaging^{12,13,14} and material sciences.^{15, 16, 17, 18} So far, the vast majority of cyanine dyes display capping groups encompassing nitrogen (**A**, Fig. 1), even though it was shown that substituting it by oxygen- or sulfur-heterocycles significantly redshifts the absorption/emission.^{19,20} During the last decades, π -systems in which the nitrogen is replaced by phosphorus, its higher group 15 analogue, became very attractive compounds. Such chromophores benefit from the particular structural and electronic features of the P atom, *e.g.*, a reactive lone pair, a pyramidal geometry preventing π -stacking, and the possibility to display σ - π conjugation.^{21,22,23} Surprisingly, while phospho-cyanines have sporadically appeared in the literature since the 1950s,^{24,25,26,27} no systematic structure-properties relationship has been established on an entire family (**B**, Fig. 1).²⁸ Actually, there is no evidence whether (pseudo)

ylidic P-C bond²⁹ would be able to generate an IPS to the corresponding structure. Interestingly whilst several articles devoted to the reactivity of organophosphorus derivatives report P-compounds fulfilling the structural requirements of phospha-cyanines (cationic compounds in which a charge is delocalized between two P over an odd number of sp^2 carbon atoms), this aspect is not commented in the articles nor the optical properties reported.^{30,31,32} In this context, we wish to highlight Yamada's approach, which studied the reaction of perfluorocyclopentene with various nucleophiles, including a phosphonium ylide, and reported a compound that can be structurally characterized as a phospha-pentamethine cyanine (Fig. 1, C, R = Ph).^{33,34} In the present contribution, we adapt this synthetic method to prepare a full family of dyes and systematically study their structures, and optical properties using a joint experimental and theoretical approach. From this study, we can conclude that these "phospha-cyanines" possess all the structural and spectroscopic properties of cyanines in their IPS.

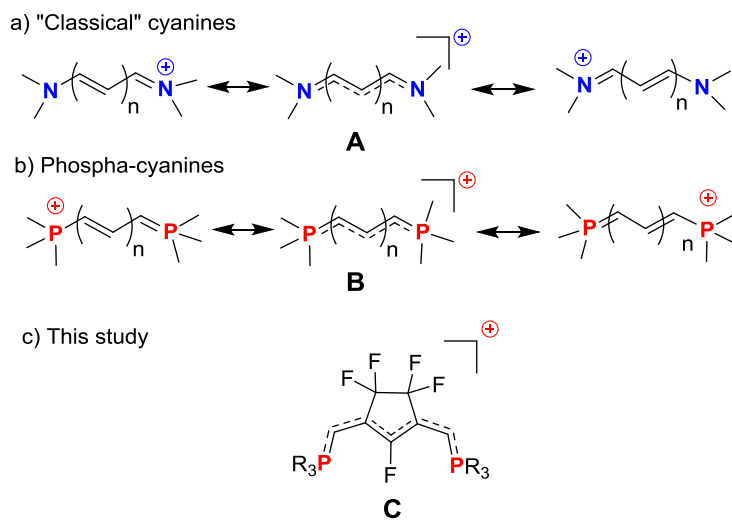


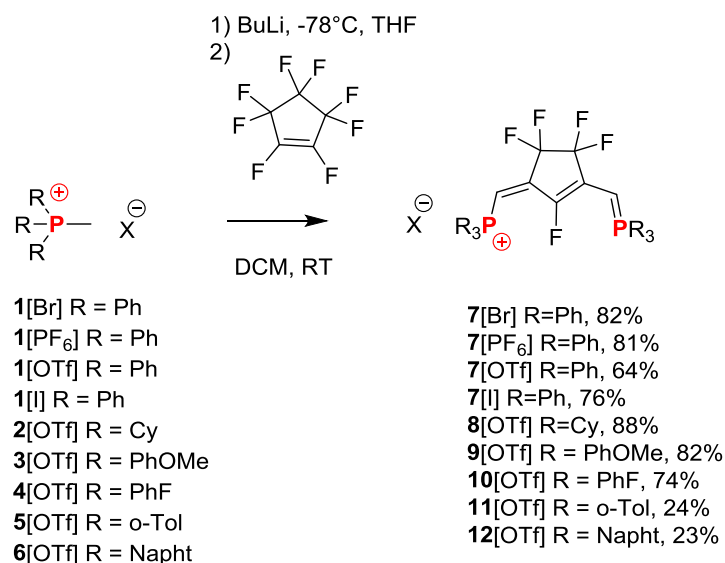
Fig. 1: General structure of "classical" cyanines **A** (a) phospha-cyanines **B** (b) dyes **C** studied herein (c).

Methods

Synthesis, full characterization, experimental and theoretical methods are described in the Supporting Information.

Results and Discussion

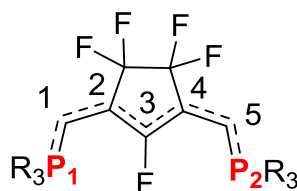
Synthesis. Penthamethines **7-12**[X] (Scheme 1) are prepared following the synthetic method developed by Yamada *et al* on **7**[X].³³ Here, a library of methyl-phosphonium **1-6**[X] are prepared from commercially available phosphanes and then converted to the corresponding phospho-cyanines **7-12**[X] upon reaction with perfluorocyclopentene. The compounds, isolated as yellow solids, are fully characterized by multi-nuclear NMR, mass spectrometry, and X-ray diffraction (see the SI). They all display a single peak in ³¹P NMR suggesting a fully symmetric structure, consistent with a cyanine in its IPS state. All the derivatives are fully stable toward air and moisture when stored as solids. The substitution of the central halogen in heptamethines is a versatile way to tune its structure.^{8,35} However, refluxing **7**[Br] in acetonitrile with piperidine only led to unreacted **7**[Br] highlighting the stability of the platform. Nevertheless, slow oxidation to the corresponding phosphine oxide was observed when the compound was stored several days in solution under ambient conditions (Fig. S56).³⁶



Scheme 1: Synthesis of **7-12**[X]

Structural characterizations. **7-11**[X] are characterized by X-ray diffraction performed on single crystals (see Fig. 2, Fig. S1-7 and Table 1 and Table S1-2). In addition, to confirm the molecular structure of the synthesized compounds, the crystallographic structure provides the opportunity to determine the BLA and therefore the “cyanine” character of the dyes.

Table 1: Crystallographic and theoretical structural data



	P1-C1	C1-C2	C2-C3	C3-C4	C4-C5	C5-P2	BLA ^c	P ₁ -C ₁ -C ₅ - P ₂
	(Å)	(Å)	(Å)	(Å)	(Å)	(Å)	(Å)	(°)
7 ⁺ _{DFT}	1.752	1.370	1.397	1.397	1.370	1.752	0	14.8
7 [Br] ³⁷	1.739(4)	1.381(7)	1.400(7)	1.382(7)	1.384(7)	1.752(4)	0.010	9.0
7 [OTf]	1.7461(14)	1.3698(19)	1.3880(18)	1.3902(19)	1.3671(18)	1.7500(13)	0.002	21.4

7 [PF ₆]	1.753(3)	1.753(3)	1.390(4)	1.389(4)	1.377(4)	1.748(3)	0.002	2.6
7 [I]	1.749(3)	1.358(4)	1.401(3)	1.375(4)	1.381(3)	1.748(2)	0.024	1.12
8 [OTf]	1.746(4)	1.384(5)	1.378(5)	1.395(5)	1.362(6)	1.766(4)	0.019	11.2
9 [OTf]	1.748(4)	1.376(6)	1.389(5)	1.395(5)	1.367(5)	1.753(4)	0.007	17.4
10 [OTf] ^a	1.733(7)	1.368(10)	1.386(10)	1.382(9)	1.383(10)	1.749(7)	0.009	1.6
	1.736(7)	1.369(9)	1.380(9)	1.403(9)	1.360(9)	1.757(7)	0.016	2.0
11 [OTf] ^b	1.747(4)	1.374(5)	1.388(4)	1.374(5)	1.374(5)	1.747(4)	0.007	8.6
	1.750(4)	1.365(6)	1.392(5)	1.392(5)	1.365(6)	1.750(4)	0	0.3
	1.749(4)	1.370(5)	1.401(5)	1.385(5)	1.369(5)	1.745(4)	0.007	19.9

^a two molecules in the unit cell ^b three molecules in the unit cell ^c defined as $BLA = |(d_{C1-C2} + d_{C3-C4})/2 - (d_{C2-C3} + d_{C4-C5})/2|$

At the molecular level, the cation always displays the *cis* geometry of the C₁-C₂ and C₄-C₅ (see Fig. 2 and Fig S1-7), consistent with the report of Yamada *et al* for [7]Br.³³ For 7⁺, DFT calculations predict the *trans* structure to be less stable by 2.6 kcal.mol⁻¹ as compared to the *cis* on the Gibbs energy scale, consistent with experimental findings. Interestingly this conformation is likely resulting from the substitution of the central moiety. Indeed, replacing the two CF₂ groups and the central fluorine atom by hydrogen atoms induce a reversal of the *cis-trans* stabilities, the latter conformer becoming more stable by 0.6 kcal.mol⁻¹ according to theory. The polymethine moiety is quasi-planar as the dihedral angle P₁-C₁-C₅-P₂ remains below 21.4°. Focussing the C-C bond lengths, in all cases, 1.358 Å < d_{C-C} < 1.401 Å and no real alternation between shorter/longer bonds is observed (see Table 1 and Fig. S8-9). This result in a BLA in the crystalline state close to 0 (BLA < 0.019 Å, see Table 1). Importantly, this absence of BLA is independent of the structure of the cation or of the counterion. DFT calculations performed in DCM provide bond distances that are close to the experimental values, the difference between measured and computed bond lengths being of the order of the impact of the counterion on the

experimental data. Similarly, the P-C bond lengths are almost identical ($1.733 \text{ \AA} < d_{\text{P-C}} < 1.753 \text{ \AA}$) and characteristic of a one and a half $\text{R}_3\text{P-C}$ bond,³⁸ with again similar DFT values. The lack of BLA change when modifying the counterion is in marked contrast to the observations made on the polymethine cyanines.^{7,39,40} This can be attributed to the bulkiness of tetravalent P atoms which prevents significant interactions between the ions. Given the impact of the anion on heptamethine dyes optical properties, the fact that phospho-cyanine conserves its IPS irrespective of the counterion is of prime importance for further applications.

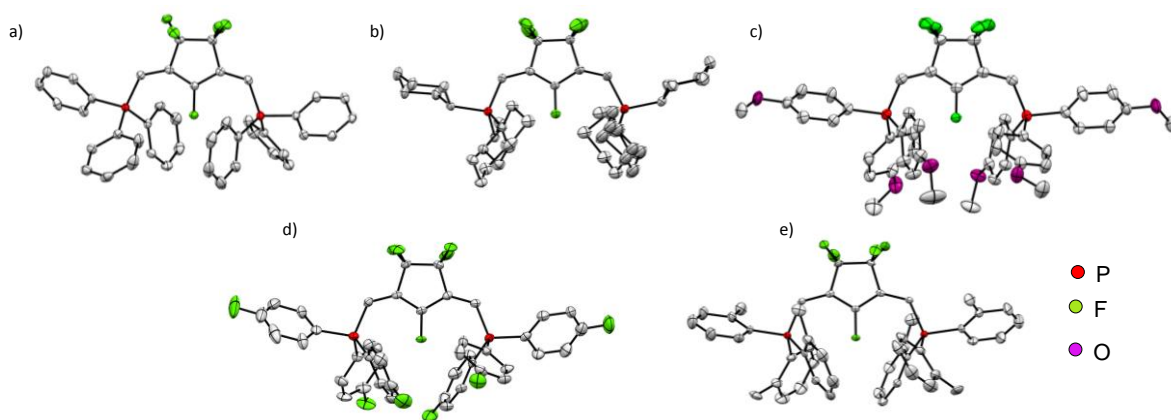


Fig. 2: X-ray structure of **7**[OTf] (a) **8**[OTf] (b) **9**[OTf] (c) **10**[OTf] (d) and **11**[OTf] (e). Hydrogen atoms and counterions are omitted for clarity and thermal ellipsoids are set at 50% probability.

Electrochemical properties. The electrochemical properties of **7-12**[OTf] were investigated by cyclic voltammetry (CV) in dichloromethane solution (Figure S17-22 and Table S3). **7**[OTf] displays quasi-reversible oxidation ($E_{\text{ox}}(\mathbf{7}[\text{OTf}]) = +0.68 \text{ V vs Fc}^+/\text{Fc}$) and irreversible reduction ($E_{\text{red}}(\mathbf{7}[\text{OTf}]) = -2.06 \text{ V vs Fc}^+/\text{Fc}$). Those potentials can be fine-tuned and the trends nicely fit with the electron richness of the lateral phosphine. The use of $\text{P}(\text{Cy})_3$ or $\text{P}(\text{PhOMe})_3$ in **8-9**[OTf]

allows for a lowering in oxidation by ~250 mV ($E_{\text{ox}}(\mathbf{9}[\text{OTf}]) = +0.42 \text{ V vs Fc}^+/\text{Fc}$) while P(PhF)₃ in $\mathbf{10}[\text{OTf}]$ raises the reduction potential by 100 mV ($E_{\text{red}}(\mathbf{10}[\text{OTf}]) = -1.95 \text{ V vs Fc}^+/\text{Fc}$).

Table 2: Spectroscopic properties.

	P-sub	$\lambda_{\text{abs}}^{\text{[a]}}$	$\epsilon^{\text{[a]}}$	$\lambda_{\text{em}}^{\text{[a]}}$	$\Phi^{\text{[a,b]}}$	$\lambda_{0,0}^{\text{[a]}}$	$\sigma^{\text{[c]}}$
		[nm]	[M ⁻¹ cm ⁻¹]	[nm]	(%)	[nm]	[cm ⁻¹]
$\mathbf{7} [\text{Br}]$	-Ph	449 ⁴¹	98000	-	-	-	-
$\mathbf{7} [\text{I}]$	-Ph	447 ⁴¹	106000	-	-	-	-
$\mathbf{7} [\text{PF}_6]$	-Ph	447	98000	-	-	-	-
$\mathbf{7} [\text{OTf}]$	-Ph	448 ⁴¹	103000	-	-	-	-
$\mathbf{8} [\text{OTf}]$	-Cy	419	105000	-	-	-	-
$\mathbf{9} [\text{OTf}]$	-PhOMe	446	132000	464	0.2	453	870
$\mathbf{10} [\text{OTf}]$	-PhF	449	97000	465	0.1	453	766
$\mathbf{11} [\text{OTf}]$	-oTol	449	106000	446	0.3	455	813
$\mathbf{12} [\text{OTf}]$	-Naphth	468	72000	494	0.6	479	1124

^a In CH₂Cl₂ (2.10⁻⁶M). ^b calculated relative to fluorescein (NaOH, 0.1 M), $\phi_{\text{ref}} = 0.79$ ^c Stokes shift in CH₂Cl₂ (2.10⁻⁶M).

Spectroscopic properties. The optical properties of $\mathbf{7-12}[\text{X}]$ were investigated in diluted CH₂Cl₂ solutions ($c = 5.10^{-6} \text{ mol.L}^{-1}$, Fig. 3, Fig. S10-17 and Table 2). All derivatives display similar absorption spectra with a sharp absorption band between 419 nm and 468 nm with high extinction coefficients (70-135 000 L.mol⁻¹.cm⁻¹) and a clear shoulder. Such band topology is typical of cyanines in their IPS, in agreement with the structural observations (see above).⁴ As evidenced in Fig. S12, no aggregation occurred in diluted DCM, as expected due to the presence of the bulky P-atom. In addition, the absorption spectra are independent of the solvent (Fig. S11). The absorption maxima are in the typical range of dimethylamino-substituted pentamethine

(Cyanine **A** (Fig.1, $n = 2$): $\lambda_{\text{abs}} = 416 \text{ nm}$)⁴², showing that the presence of P does not break the conjugation along the polymethine bridge. For comparison purpose, we computed the dimethylamino-analogs of 7^+ (*trans*-**N7**⁺ and *cis*-**N7**⁺, see Fig. S28). Interestingly, while all calculated vertical absorptions are comparable, the EDD of **7-12**⁺ display a reverse electronic distribution with a loss of density on the central C-F fragment (Fig. 4 and 5), while *cis*-**N7**⁺ shows the classical cyanine pattern with a gain of density on this central C (Fig. 5). Such difference in electronic behaviour is linked to the nature of the lateral groups (R_2N^- for *cis*-**N7**⁺ vs Ph_3P^+ for 7^+). Hence, in classical cyanine dyes such **A** or *cis*-**N7**⁺, the positive charge is delocalized between the two N-lone pairs, while in phosphacyanines such as 7^+ , due to the ylidic nature of the lateral fragment, the charge mostly delocalized between the C adjacent to P. This particular electronic configuration was confirmed on the hypothetical analog of 7^+ displaying Ph_3N^- end groups (Fig. S30).

Surprisingly, the effect of substituents (either electron-donating -OMe or electron-withdrawing -F) on the phenyl ring attached to the P is trifling ($\lambda_{\text{abs}}(\mathbf{7}[\text{OTf}]) = 448 \text{ nm}$, $\Delta\lambda_{\text{abs}}(\mathbf{7-9-10-11}[\text{OTf}]) = 3 \text{ nm}$). However, when the nature of the substituent is changed (Cy vs Ph vs Napht), the impact on the absorption wavelengths becomes more significant as the maximal absorption wavelengths shift from $\lambda_{\text{abs}}(\mathbf{8}[\text{OTf}]) = 419 \text{ nm}$ to $\lambda_{\text{abs}}(\mathbf{12}[\text{OTf}]) = 468 \text{ nm}$. We have performed theoretical calculations to probe the nature of the excited states of these systems. The protocol is detailed in the SI, and goes beyond standard TD-DFT using wavefunction theories for transition energies, as cyanines are known to be challenging for this level of theory.⁴³ The vertical absorption wavelength computed is 408 nm for 7^+ logically blue shifted as compared to experiment (see below). More interesting is that very similar wavelengths are determined for 9^+ (410 nm), 10^+ (415) nm, and 11^+ (404 nm), whereas significantly smaller and larger absorption wavelengths are

respectively predicted for $\mathbf{8}^+$ (387 nm) and $\mathbf{12}^+$ (439 nm), in perfect agreement with the experiments. Fig. 4 displays the frontier orbitals and electron density difference (EDD) plot for $\mathbf{7}^+$. Consistent with a cyanine nature, the EDD plot displays an alternation on odd/even carbon atoms that undergo large decrease/increase of electronic density upon absorption. The changes of density on the atoms not involved in the cyanine moiety are essentially negligible but for the fluorine atom attached to the central carbon atoms that acts as a secondary donor group. The LUMO is nevertheless slightly delocalized on the side phenyl rings. In Fig. S24, the same representation is given for $\mathbf{8}^+$ and $\mathbf{12}^+$ and one notes similar topologies for the EDD and MOs, which respectively slightly less and more delocalized LUMO as compared to $\mathbf{7}^+$.

More quantitative theory experiment can be reached by considering 0-0 energies (for emissive dyes) and band shapes. For the latter, one can find in Fig. S25 the theoretical band shape of $\mathbf{7}^+$, and it clearly fits the experimental one with a marked shoulder and a molar extinction coefficient fitting the experimental value as well. As 0-0 energies, theory returns 2.69 eV, 3.17 eV, 3.00 eV, 2.88 eV, 3.06 eV, and 2.99 eV in the $\mathbf{7}^+$ to $\mathbf{12}^+$ series. For the three cases in which it can be compared to experiment, namely $\mathbf{9}^+$, $\mathbf{10}^+$, and $\mathbf{12}^+$, the discrepancies between theory and experiment are of the order of 0.2-0.3 eV, which is usual for such level of theory.⁴³

It has been shown on various cyanine dyes that the nature of the counterion strongly impacts the absorption in apolar solvents and in solid state.^{15d,39} Here, neither the band shape nor the absorption wavelength are affected by the nature of the counterion (Fig. S11). However, a small variation of extinction coefficient is observed (Table 2), but in all cases high values ($\sim 100000 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) characteristic of cyanine dyes in their IPS are observed.⁴⁴ The absence of strong ionic interaction even in toluene solution (Fig. S10) is due to the bulkiness of the tetravalent P-atom which prevents the ions to strongly interact, in contrast to the “classical” cyanines, in full

agreement with the structural study based on X-ray diffraction (*vide supra*). This feature is a clear advantage for considering further applications in the solid state (see for example in PMMA thin films, Fig. S13), as the absorption properties will be similar to those in diluted solution. No complex anion engineering will thus be necessary to maintain the cyanine behaviour.

Finally, emission could be recorded for some compounds (Table 2 and Fig. 3, Fig. S14-17). If the associated luminescence quantum yield remains poor ($\phi < 0.5\%$), the measured Stokes shift is small, again fitting the cyanine structure. The trend observed in luminescence wavelengths follows the one observed in absorption. We have used theory to obtain some first hints on this absence of emission, or very low ϕ . First, optimization of the lowest excited-state of 7^+ starting from the Franck-Condon geometry yields a stable local minimum quite close to the ground-state geometry. This minimum remains a bright state with an oscillator strength larger than 0.5 with both TD-DFT and CC2, indicating that there is no dark state quenching appearing in the excited state, consistent with the experimentally measured small Stokes shifts (for the emissive dyes). Second, given the presence of “heavy” phosphorous atoms, we envisaged the possibility of intersystem crossing (ISC). Theory returns only one triplet below the lowest singlet (on the S_1 optimal geometry), but this triplet is both strongly energetically far ($\Delta_{ST} = 0.77$ eV) and weakly coupled (SOC of 0.22 cm^{-1}) with the corresponding singlet, which is not favorable for ISC. Third, we have computed the radiative and internal conversion rates on the basis of our vibronic calculations (see the SI for details). This yields a large k_r of $2.18 \cdot 10^8$ s^{-1} and a smaller k_{ic} of $1.10 \cdot 10^8$ s^{-1} meaning an estimated fluorescence yield of 66%, obviously inconsistent with experiment, indicating that internal conversion is not the only non-radiative pathway. The logical fourth step was to search for the S_1/S_0 minimum energy crossing point (MECP) for this molecule. As can be seen in Fig. S25-26, the MECP we identified corresponds to the twisting of one lateral R₃PCH-

group by ca. 90° with respect to the central ring. This MECP is located more than 1 eV below both the Franck-Condon point and the above-mentioned local S_1 minimum, clearly easily accessible. This explains the observed quenching of emission: there is a very low-lying crossing point between the excited and ground-state potential energy surfaces offering an efficient non-radiative deactivation pathway.

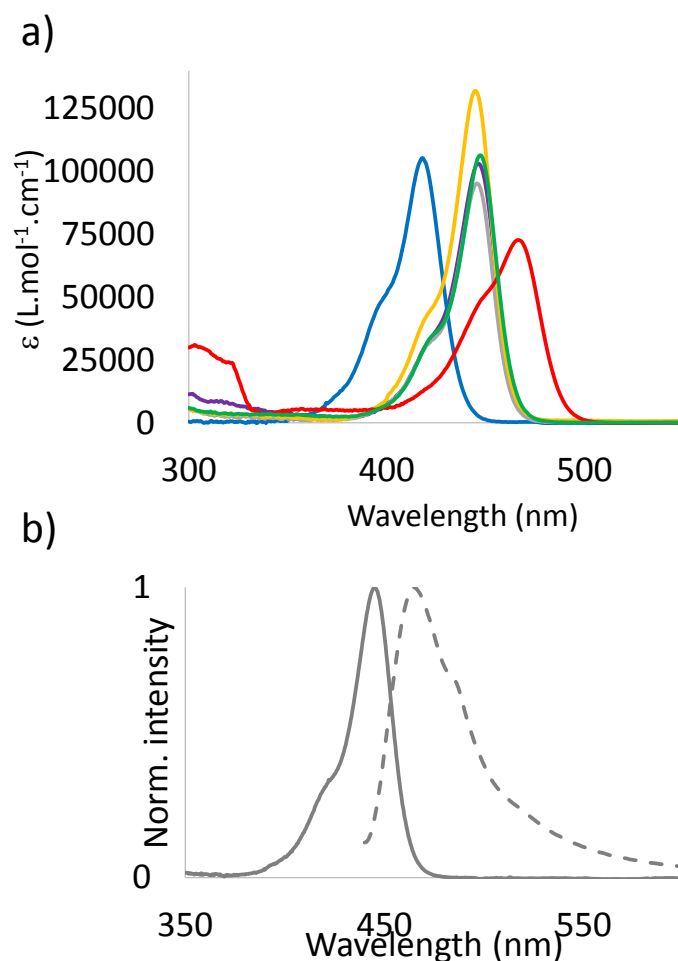


Fig. 3: a) absorption of 7[OTf] (purple), 8[OTf] (blue), 9[OTf] (grey), 10[OTf] (orange), 11[OTf] (green) and 12[OTf] (red) in diluted DCM solution ($c= 3 \cdot 10^{-6}\text{M}$) (up); b) normalized absorption and emission spectra of 10[OTf] in diluted DCM ($c= 3 \cdot 10^{-6}\text{M}$)(down)

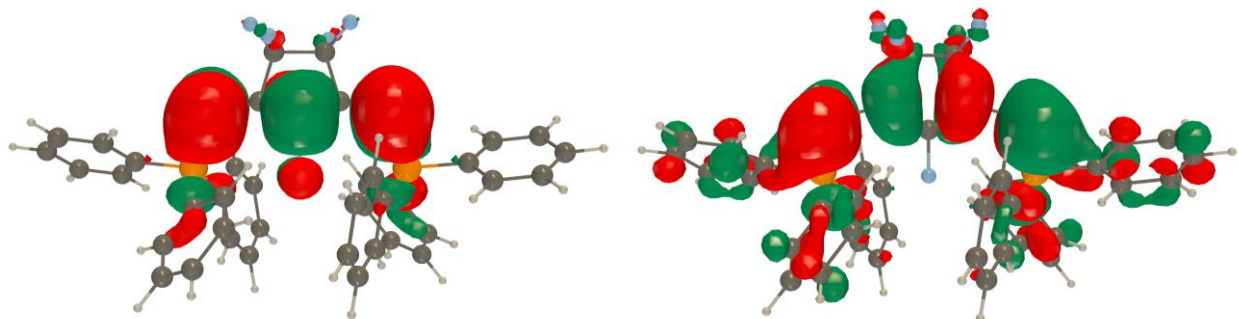


Fig.4. HOMO (left) and LUMO (right) plots for 7^+ using a contour threshold of 0.02 au.

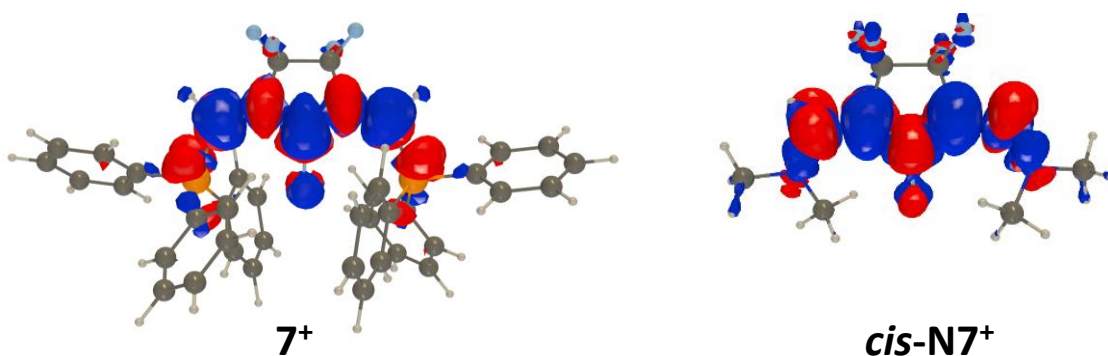


Fig.5. EDD plots for 7^+ (left) and *cis-N7*⁺ (right) using a contour of 0.001 au. Blue and red zones respectively represent regions of decrease and increase of density upon excitation.

Conclusion

In this article we report the synthesis and full characterization of a family of phosphapentamethine cyanines **7-12**[X]. These cationic dyes are prepared in only two steps starting from commercial phosphanes. The impact of the P-substituents and the counterions on the structural and optical properties is investigated using a joint experimental/theoretical approach. All the

phospha-cyanines present a BLA close to zero according to the crystallographic structures, confirming their Ideal Polymethine State (IPS). All these compounds display a sharp UV-vis absorption band with a vibronic shoulder, characteristic of a cyanine in its IPS. However, a reverse electronic configuration compared to classical cyanines is observed. The low luminescence quantum yield was rationalized on the basis of TD-DFT calculations. Interestingly, the optical properties of these phospha-cyanines are independent of both the solvent and the counterion. This is contrast in to its N-analogs and enables predictive engineering of the phospha-cyanines regardless of the medium in which they are used (biological media or materials) which is a clear advantage for potential applications. Finally, this study also paves the way toward the preparation of unprecedented cyanines dyes featuring heavier main-group elements, as those heteroatoms were recently described to induce unusual structural/electronic properties to chromophore/fluorophores.^{45,46,47}

Supporting Information description.

Synthetic procedure, complete characterizations, X-ray crystallographic data and CIF files, computational details and Cartesian coordinates. The following files are available free of charge.

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