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Expanded Pyridiniums: Bis-cyclization of Branched Pyridiniums into Their Fused Polycyclic and Positively Charged Derivatives—Assessing the Impact of Pericondensation on Structural, Electrochemical, Electronic, and Photophysical Features

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Abstract: This study evaluates the impact of the extension of the π -conjugated system of pyridiniums on their various properties. The molecular scaffold of aryl-substituted expanded pyridiniums (referred to as branched species) can be photochemically bis-cyclized into the corresponding fused polycyclic derivatives (referred to as pericondensed species). The representative 1,2,4,6-tetraphenylpyridinium $(1^{\rm H})$ and 1,2,3,5,6-pentaphenyl-4-(p-tolyl)pyridinium (2^{Me}) tetra- and hexabranched pyridiniums are herein compared with their corresponding pericondensed derivatives, the fully fused 9-phenylbenzo[1,2]quinolizino[3,4,5,6def]phenanthridinium (1^Hf) and the hitherto unknown hemifused 9-methyl1,2,3-triphenylbenzo[h]phenanthro-[9,10,1-def]isoquinolinium (2^{Me}f). Combined solid-state X-ray crystallography and solution NMR experiments showed that stacking interactions are barely efficient when the pericondensed pyridiniums are not appropriately substituted. The electrochemical study revealed that the first reduction process of all the expanded pyridiniums occurs at around -1 V vs. SCE, which indicates that the lowest unoccupied molecular orbital (LUMO) remains essentially localized on the pyri-

Keywords: electrochemistry • fused-ring systems • luminescence • pyridiniums • star-shaped molecules dinium core regardless of pericondensation. In contrast, the electronic and photophysical properties are significantly affected on going from branched to pericondensed pyridiniums. Typically, the number of absorption bands increases with extended activity towards the visible region (down to ca. 450 nm in MeCN), whereas emission quantum yields are increased by three orders of magnitude (at ca. 0.25 on average). A relationship is established between the observed differential impact of the pericondensation and the importance of the localized LUMO on the properties considered: predominant for the first reduction process compared with secondary for the optical and photophysical properties.

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- Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201000504. Details of the synthesis and characterization of new compounds and precursors including ¹H (500 MHz) and ¹³C NMR (126 MHz) spectra as well as ESI-mass spectra, ORTEP drawings of various X-ray structures, selected cyclic and square wave voltammograms, study of the impact of concentration on the electrochemical behavior of **1**^H and **1**^H*f*, electronic absorption spectra of pyrylium precursors.

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Introduction

The present work assesses the extent to which pericondensation^[1] of the branched molecular scaffold of aryl-substituted pyridiniums can improve^[2] not only their electrochemical features as electrophores^[3] but also their electronic and photophysical properties as chromophores and luminophores, respectively.

In their various forms, pyridinium salts are ubiquitous, whether taking part in natural processes, as in the case of the NAD⁺/NADH cofactor,^[4] or serving as functional elements in the multifaceted fields of chemistry.^[5] Beyond their widespread use as a result of their cationic charge, pyridiniums are essentially valued 1) for their electron-withdrawing properties ("pull" effect) as part of chromophores (especially solvatochromic dyes)^[6,7] and NLO-phores (push–pull assemblies)^[8] and 2) for their electron-accepting (redox) properties as electrophoric subunits.^[9-11] However, with the notable exceptions of zwitterionic pyridinium *N*-phenoxide dyes (Reichardt's salts)^[6a] and other heterocyclic mesomeric betaines,^[12] the electronic and redox^[13] properties of pyridiniums themselves are rarely finely tuned with substituents.

With regard to the electrochemical properties of pyridiniums, the most popular strategy for their enhancement involves arranging their oligomers and especially dimers in close covalent assemblies to take advantage of their mutual electronic and electrostatic influences.[14-18] Fine-tuning of the electrochemical properties of the dimers can be achieved by varying the following parameters:^[18a,19] 1) The interannular dihedral angle (that is, the degree of π delocalization),^[20] 2) the connection scheme of the pyridinium rings, 3) the nature of the $N_{pyridinio}$ substituent (alkyl or aryl),^[14] and 4) the nature of the intervening linker (if any),^[21] which can even be switchable.^[22] The same approaches also hold for higher oligomers, even incorporating intervening spacers^[19] like star-shaped tris-^[23] and hexakis(*p*-*N*-alkylpyridinium)benzene^[24] or other discrete entities like linear polypyridinium wires,^[25,26] polyviologen dendrimers^[27] and rodlike (1D) polymers.^[28,29]

Interestingly, another strategy exists for manipulating the redox features of certain classes of molecules and polymers. This approach is aimed at promoting extended π systems to enhance π delocalization.^[30] Typically, molecules like benzene or pyromellitic diimide can be expanded towards hexaperi-benzocoronenes and graphenes^[31] for the former and perylene-, terrylene-, quaterrylene diimides,^[32,33] and higher extended rylenebis(dicarboximide)s^[34] for the latter. In the case of polyimide acceptors, it is known that the first reduction potential becomes more positive (that is, more easily accessible) as the "core aromatic ring system becomes larger".^[33,35,36] Whether the same trend is observed or not for the pyridinium series deserves verification in the context of efforts directed towards the improvement^[2] of their efficiency as electrophores. Enhancing π extension and delocalization usually also has an impact on the electronic and photophysical properties of expanded fused molecules (as chromophores and luminophores, respectively). However, this approach remains underexploited for pyridiniums,^[37] whether for electrochemical,^[19] electronic, or photophysical properties.

In the framework of our research devoted to the controlled formation of charge-separated states within well-defined photosensitizer-acceptor covalent dyad assemblies, we have developed monocationic tetraarylpyridinium (" TP^+ ") groups (1^{R2} in Scheme 1) as the electron-acceptor compo-



Scheme 1. General representation of the tetra-branched pyridiniums $[R^0ph-TPR^1_2R^2]^+$ and the photochemically generated fused $[R^0-fTPR^1_2-phR^2]^+$ species. The two expanded pyridiniums investigated here $(R^0, R^1, R^2=H)$ are labeled as 1^H and 1^Hf .

nent.^[38] We are now interested in the fused ("f") derivatives of these tetraarylpyridiniums ($1^{R2}f$ in Scheme 1). First reported by Katritzky and co-workers three decades ago,^[39] organic species of the type $1^{R2}f$ have not attracted the attention deserved. This is surprising as examples of fused polycyclic molecular scaffolds comprised of a centrally positioned cationic charge are quite rare in the literature.^[37,40,41]

As a first step towards the use of pericondensed species $(1^{R2}f)$ as electron and/or energy acceptors within covalent assemblies, we have undertaken the detailed study of the simplest representative element of the series, namely the 9-phenylbenzo[1,2]quinolizino[3,4,5,6-*def*]phenanthridinium (noted $1^{H}f$ in Scheme 1), which was compared with its parent branched precursor 1,2,4,6-tetraphenylpyridinium (noted 1^{H}).

We also synthesized and investigated the simplest representative element of the hitherto unknown class of pericondensed and hemifused ("hf") species (i.e., $2^{R2}f$), that is, 9methyl-1,2,3-triphenylbenzo[h]phenanthro[9,10,1-def]isoquinolinium (labeled $2^{Me}f$ in Scheme 2). This molecule is photochemically derived from hexaaryl-substituted pyridiniums (" XP^+ " type in Scheme 2) and more precisely from 1,2,3,5,6-pentaphenyl-4-(p-tolyl)pyridinium (noted 2^{Me} in Scheme 2).

In this paper we report on the intrinsic properties of these two classes (branched and fused) of expanded pyridiniums with a view to optimizing their future use. It is important to note that in contrast to the tetra-branched pyridiniums (1^{R2}) ,^[42] virtually nothing is known about the electrochemical, electronic, and photophysical properties of hexabranched pyridiniums $(2^{R2})^{[43]}$ and pericondensed $(1^{R2}f$ and $2^{R2}f$) expanded pyridiniums. The propensity of fused species to undergo stacking has also been assessed because aggregation in solution is likely to complicate the proper determina-

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Scheme 2. General representation of the hexa-branched pyridiniums $[R^0ph-\mathbf{XPR}^1_2R^3_2R^2]^+$ along with the hemifused derivatives $[R^0ph(R^1ph)_{2^-}hf\mathbf{XPR}^3_2R^2]^+$. The four expanded pyridiniums investigated here $(R^0, R^1, R^3=H \text{ and } R^2=H, Me)$ are labeled as follows: 2^{H} , $2^{H}f$ and 2^{Me} , $2^{Me}f$. Compounds 2^{Me} , $2^{Me}f$, and $2^{H}f$ are new species.

tion of the genuine molecular properties of expanded pyridiniums beyond the potential interest of this phenomenon for the construction of self-assembled hierarchical molecular materials.^[44,45]

Here we show that pericondensed pyridiniums are not better electrophores than the parent branched species. From a more general viewpoint, depending on whether a given molecular property better fits a delocalized or localized description, extending the π system of a pyridinium by pericondensing its aryl branches will naturally impact or not this property. We demonstrate that the presence of the cationic heteroatom (i.e., the charged iminio site) imposes the reactivity typical of the pyridinium ring as a prevailing pattern, that is, a localized description as far as the electrochemistry is concerned, regardless of the degree of π extension. This is not the case for the electronic and photophysical features. In addition, the hitherto unknown properties of hexabranched pyridinium (2^{R2}) are disclosed.

Results and Discussion

Synthesis: N_{pyridinio}-Aryl-substituted (R⁰-ph) polyarylpyridiniums, including the subclasses of tetraaryl- ($[R^0ph-TPR_2^1R^2]^+$) and hexaaryl- ($[R^0ph-XPR_2^1R_2^3R^2]^+$) expanded pyridiniums $(1^{R_2} \text{ and } 2^{R_2} \text{ in Schemes 1 and 2})$, were obtained by treating conveniently substituted arylamine (R^0 ph-NH₂) with the appropriately decorated triaryl- and pentaaryl-substituted pyrylium salts $[\mathbf{TPyrR}_{2}^{1}\mathbf{R}^{2}]^{+}$ and $[\mathbf{PPyrR}_{2}^{1}\mathbf{R}_{2}^{3}\mathbf{R}^{2}]^{+}$, respectively (see the Supporting Information). Procedures for the synthesis of the pivotal pyrylium precursors in general are well documented.^[46] Triarylpyryliums ($[TPyrR_2^1R^2]^+$) were readily synthesized in one step from the appropriately substituted benzophenone (\mathbf{R}^1) and benzaldehyde (\mathbf{R}^2) in the presence of phosphorus oxychloride. The pentaaryl salt $[\mathbf{PPyrR}_{2}^{1}\mathbf{R}_{2}^{3}\mathbf{R}^{2}]^{+}$ required a two-step process: Synthesis of the diketone precursor^[47] followed by intramolecular dehydration. The latter dehydrogenative cyclization was performed in the presence of triphenylcarbenium as hydride abstractor (see the Supporting Information).^[48,49]

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Aryl-aryl bond formation within branched pyridiniums was performed photochemically (Scheme 1 and 2) following the procedure originally perfected by Dorofeenko^[50] and Katritzky^[39] and their co-workers, who were the first to synthesize $1^{H}f$ in the late seventies along with numerous other $[\mathbf{R}^0 - \mathbf{fTPR}^1 - \mathbf{phR}^2]^+$ derivatives (\mathbf{R}^0 , \mathbf{R}^1 , and \mathbf{R}^2 in Scheme 1). Basically the rings were fused by a photochemical cyclodehydrogenation process rationalized by Mallory^[51] and Katz^[52] and their co-workers for the photocyclization of stilbenes into fused phenanthrene derivatives. This photoconversion requires the presence of an oxidizing agent such as molecular dioxygen (present case) or iodine (I₂). There also exists a purely chemical route to fused polycyclic aromatic hydrocarbons (PAH) deprived of positively charged heteroatoms, which essentially relies on the so-called Scholl reactions popularized by Müllen and co-workers^[53] for the synthesis of benchmark hexa-peri-hexabenzocoronene (HBC) derivatives.^[54] The widely used oxidative version of this chemical approach was found to be ineffective in our hands. For example, among other trials, we treated reference species 1^{H} and $2^{Me}f$ (to further fuse the molecular scaffold) according to the well-established procedure based on the use of anhydrous FeCl₃ in a mixture of CH₃NO₂ and CH₂Cl₂ at room temperature,^[55] but we finally only recovered the starting material with exchanged counteranions (see the crystal structures of $[2^{Me}f](FeCl_4)$ and $[2^{Me}f]Cl$ in the Supporting Information). The complexity of these reactions based on the combined use of Lewis and/or Brønsted acids, oxidants (or reducing agents), and so forth has been highlighted in a few theoretical studies.[56,57]

Note, when adding two aryl groups at the meta positions of the pyridinium core, that is, going from tetra-branched $(1^{R2}, Scheme 1)$ to hexa-branched $(2^{R2}, Scheme 2)$, the site of photoinduced cyclodehydrogenation is shifted from the $N_{\rm pyridinio}$ -aryl group towards the tolyl terminus at the 4-position of the pyridinium ring. Although this finding is, at first glance, in contradiction with the conclusions of the studies of Katritzky and co-workers, which suggest that electron-donating substituents disfavor (or deactivate) photochemical cyclodehydrogenation,^[39] it is, however, in line with another particular observation by the same author that "where the possibility exists of alternative cyclizations to a phenyl or a *p*-tolyl group, the latter seems to be preferred".^[39b] This is the case for $2^{Me}f$, which is by far the main photoproduct as judged from the ¹H NMR spectrum of the reaction's crude (see Figure S-VIIa in the Supporting Information). Note that here the methyl substituent is first used as an internal probe for ¹H NMR characterization. A control experiment performed on hexaphenylpyridinium 2^{H} (i.e., the hexabranched pyridinium deprived of methyl as the R² substituent) also yielded the corresponding hemifused species $2^{H}f$ as the major, and even only, identified photoproduct (see the informative ¹H NMR (Figure S-IXa) and mass spectra (Figure S-XXIg) of the photoreaction crude in the Supporting Information). Thus, the contribution of the methyl as a weak inductive electron donor is ruled out. Also note that ring fusion does not proceed for all of the six pendant aryl

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groups, but stops after two C–C bonds have been formed around the aryl- R^2 terminus (whether R^2 is Me or H, Scheme 2). In the following, we refer to these partly fused products as hemifused species $2^{R^2}f$. Incomplete pericondensation is rationalized in terms of competing processes of ultrafast intramolecular energy transfers and cyclodehydrogenation on the one hand and existing intramolecular constraints in the hemifused species on the other (see General Comments below).

Expanded pyridiniums as molecular platforms-insights into the ground-state structural features of pericondensed species: The precise determination of the structural features of molecules is of importance not only when dealing with molecules in the ground state, for instance, to assess their ability to self-assemble within supramolecular architectures, but also when exploring their electrochemical, electronic, and photophysical properties. Conformational changes following reduction or excited-state charge or spin-density redistribution can be huge^[58,59] and must be taken into account for semi-rigid molecules like those investigated herein. Induced structural changes can alter the electrochemical behavior of electrophores, whether the reversibility of redox processes or the driving force of photoinduced electron transfer (PET), when the reorganization energy is large. Structural fluctuations can also appear as vibronic contributions likely to impact the absorption spectra of the chromophores as well as significant Stokes' shifts or changes in emission quantum yields (relative efficiency of nonradiative decay pathways) subsequent to photoexcitation, which are key features of luminophores. These various and inter-related aspects are investigated below.

Ground-state structural characterization—insights from a solid-state study (X-ray analysis): The ORTEP diagrams in Figures 1 and 2 show the salient structural features of the two types of pericondensed pyridiniums $1^{R2}f$ and $2^{R2}f$.

Crystals of $[1^{H}f](BF_{4})$ grown from acetonitrile afforded a solvated structure, $[1^{H}f](BF_4)$ ·CH₃CN (Figure 1), which can be termed a pseudopolymorph of the structure recently reported by Müllen and co-workers^[45] (compound 1 in the reference, grown from methanol) for the same, but nonsolvated, BF₄⁻ salt. The crystal structure of this nonsolvated BF₄⁻ salt (the crystal of 1) consists of "tail-to-tail" stacks of planar $1^{H}f$ molecules, which are organized as layers.^[45] On the other hand, the orthorhombic structure of the acetonitrile-solvated BF4- salt [1Hf](BF4)·CH3CN reported herein displays columnar packing made up of $1^{H}f$ molecules stacked in a cofacial "head-to-head" manner (Figure 1). This packing closely resembles that of the crystal structure of the methanol-solvated benzenesulfonate (PhSO₃⁻) salt of $1^{H}f$, also reported by Müllen and co-workers^[45] (compound 2) in the reference). In $[1^{H}f](BF_4) \cdot CH_3CN$, the columnar stacks are indeed arranged in a herringbone^[60] fashion rather similar to that found in the PhSO3⁻ structure, albeit the angle between the stacks is less pronounced in the latter case. In contrast to the PhSO₃⁻ salt,^[45] but similarly to the BF₄⁻ nonsolvated pseudopolymorph (compound 1),^[45] no bending of the molecular scaffold is observed in our case in the solid state for reasons of crystal symmetry. Indeed, the main molecular axis lying along the C-C bond connecting the fused polycyclic fragment of $1^{H}f$ and its phenyl terminus is parallel to the [001] crystal axis.

To summarize, the structural analysis shows that $[1^{H}f]$ -(BF₄) salts may display completely different crystal packing (e.g., layered versus columnar) depending on the solvent



Figure 1. ORTEP diagrams of $[1^{H}f](BF_4)$ -CH₃CN with thermal ellipsoids (50% probability). a) Top and b) side views of the $1^{H}f$ molecular unit and c) top and d) side views of the cofacial "head-to-head" layout of two π -stacked molecules.

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used for crystallization (e.g., methanol versus acetonitrile) and the level of solvation and regardless of the nature of the counteranion (whether the same, here BF_4^- , or different, for example, $PhSO_3^-$). This finding makes questionable the relevance of the recently reported strategy^[45] for controlling the crystal packing of naked **1**^H*f* molecules by relying on the nature of counteranions.

Note also that the interplanar distance (3.39 Å) between two stacked $\mathbf{1}^{H} f$ fused molecules does not significantly vary on passing from the cofacial "head-to-head" layout to the cofacial "tail-to-tail"^[45] layout, falling in the usual range for both the pure, neutral PAHs^[61,62] (ca. 3.4-3.5 Å) and the planar carbeniums of the TOTA type^[41] (ca. 3.3-3.4 Å). Therefore if the coulombic repulsion between adjacent cationic N_{pyridinio} atoms (which are 4.249 Å apart)^[63] is operative within the "head-to-head" columnar stacks, its destabilizing contribution is more than compensated by stabilizing forces such as π - π interactions involving six fused rings per molecule (versus the only two rings of pendant phenyl and pyridinium for the "tail-to-tail" dimer) and cation- π interactions^[64] (not present in the "tail-to-tail" dimer). This is all the more the case as the pericondensed pyridiniums are segregated from their fluorinated counteranions (see the Supporting Information) thereby hindering the shielding role of BF₄⁻ with respect to the abovementioned electrostatic interaction.

With regard to the hemifused species $2^{Me}f$ we solved three X-ray structures (all monoclinic) with different counteranions (BF₄⁻, FeCl₄⁻, and Cl⁻), which allowed us to derive some general structural trends (Figures 2 and 3 see also the Supporting Information).

The planarity of the fused core noted for $1^{H}f$ is lost in the case of the hemifused species $2^{Me}f$, which is strongly distorted. In fact, only slight conformational variations of the three pendant aryl rings are observed whereas the bending deformation of the fused polycyclic fragment remains virtually the same for all four characterized $2^{Me}f$ motives,^[65] regardless of the crystal packing, the nature of the counteranions, and the presence of co-crystallized solvent molecules (Figure 3). This finding strongly suggests that the origin of this deformation is related to intramolecular structural constraints, which include the steric hindrance caused by the dangling rings.

The sandwich-herringbone^[60] packing of the hemifused species does not appreciably change as a function of the nature of the counteranions or the co-crystallized solvent molecules when present. However, contrary to the case of $[1^{H}f](BF_{4})\cdot CH_{3}CN$, no columnar π - π stacking was found in any of the three structures solved, but one-dimensional protodimeric associations instead (Figure 2). In the crystal structures of both $[2^{Me}f](BF_{4})\cdot 1.64H_{2}O$ and $[2^{Me}f](FeCl_{4})$, the $2^{Me}f$ molecules indeed form head-to-head pseudodimers. The associated molecules mutually exhibit opposite curvatures because they are actually symmetry-related through an inversion center with their counteranions lying between molecular assemblies.

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Figure 2. Selected ORTEP diagrams representing the structures of $2^{Me}f$: top) $2^{Me}f$ molecular unit and associated counteranion (from $[2^{Me}f](FeCl_4)$) and bottom) the head-to-head dimer (from $[2^{Me}f](BF_4)$ -1.64H₂O).



Figure 3. Superimposed molecular backbones of four independent 2^{Mef} units issued from the three structures solved with different counteranions: BF_4^- , $FeCl_4^-$, and Cl^- . Hydrogen atoms and counteranions have been omitted for clarity.

Ground-state structural characterization—insights from a solution NMR study: Concentration measurably impacts on the NMR spectra of pericondensed species like $1^{H}f$, as shown in Figure 4. We therefore investigated the effect of concentration not only to allow direct comparison of various pyridiniums without bias, but also to gain insights into possible preferential interactions (e.g., self-assembling processes) that could take place, as has already been reported for this type of molecule.^[40,44]

At first glance the marked and similar sensitivities of the protons A3-H, C6-H, C3-H, B3-H, and B4-H towards solution concentration (Figure 4) is compatible with the impact

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Figure 4. Concentration (c, mM; in CD₃CN) dependence of the ¹H NMR (500 MHz) spectra of $[1^{H}f](BF_{4})$.

of the formation in solution (at high concentrations) of cofacial "head-to-head" or "tail-to-tail" dimers or oligomer assemblies according to the layouts evidenced in the solidstate, whether in the present work (see Figure 1) or in the recent report by Müllen and co-workers.^[45] However, from homonuclear ¹H,¹H NOESY measurements, only intramolecular and no intermolecular through-space nuclear Overhauser effects (NOEs) related to existing π -stacked dimers or oligomers could be detected in the favorable case of concentrated (and even saturated) acetonitrile solutions (Figure S-IVb in the Supporting Information).^[66] Note also that the signs of the NOE cross-correlations are positive and that no sign inversion or change in the relative intensities is observed for the whole range of concentrations investigated (Figures S-IVc and IVd in the Supporting Information). This finding indicates that if aggregation takes place in solution, the weight of assemblies should be less than 1000 Da (for a 500 MHz proton Larmor frequency at 300 K),^[67] which corresponds to π stacks made up of three 1^H f molecules at the maximum. Finally, the absence of variation of line-broadening with concentration is also consistent with the absence of significant aggregation in solution. Therefore the marked concentration dependence of the chemical shifts of certain protons may be due to the combined effects of some loosely defined $\pi - \pi$ interactions (and slight aggregation) as well as to some kind of ion-pairing impacting on the interannular dihedral angle (similar to those observed for unfused precursors), which are both essentially present at high concentrations. Whether the cationic charge embedded within fused polycyclic fragments is sufficient to destabilize the π - π stacks (electrostatic repulsion) or the presence of a ball-shaped counteranion in the direct (apical) vicinity of the N_{pyridinio} atom merely precludes large aggregation remains unclear.

To summarize, no massive self-assembly is directly observed for bare $1^{H}f$ molecules, contrary to the cases reported by Müllen and co-workers^[40,44] with $1^{H}f$ molecular platforms bearing long alkyl chains as the $N_{\text{pyridinio}}$ -R⁰ substituent (R⁰= C_6H_{13} and $C_{14}H_{29}$; Scheme 1). Beyond the nature of both the solvent (methanol instead of acetonitrile) and the counteranions, the presence of these lipophilic decorations is crucial for the formation of supramolecular assemblies. On the other hand, a poor propensity to participate in intermolecular inter-

actions in solution facilitates the proper (safe) characterization of the intrinsic properties of fused species as model acceptors (electrophores) and chromophores/luminophores.

With respect to the $2^{Me}f$ hemifused species, intramolecular NOEs involving protons of the terminal methyl and vicinal protons D3-H of the fused moiety allowed the identity of the molecule to be confirmed (Figure S-VIId of the Supporting Information), in particular, with regard to the site of biscyclization (R² side instead of the R⁰ side, as in $1^{H}f$). As in the previous case, no intermolecular NOEs could be detected although a sizable dependence of the ¹H NMR pattern upon concentration was observed (Figure S-XXVI in the Supporting Information).

Expanded pyridiniums as electrophores—ground-state redox properties: The main question assessed in this section is whether or not reduction potentials become more accessible (anodic shift) upon pericondensation of branched pyridiniums. In other words, the aim is to determine whether or not the LUMOs attached to expanded pyridiniums lie at lower energies^[37] than in the parent branched molecules. The reversibility of the first reduction process(es), which is also a key parameter for electrophores, is also discussed for each pyridinium.

The electrochemical properties of the various pyridinium derivatives (branched and fused) synthesized in this work are presented in Table 1.^[68,69]

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Table 1. Electrochemical data and assignment of redox processes for the examined pyridiniums in dry acetonitrile with $0.1\,{\rm M}$ $TBAPF_6$ at a platinum electrode.^{[a]}

Entry	Electrophore ^{+//}	Electrophore ^{0/-}			
2	$E_{1/2}$ [V]	n	$E_{1/2}\left[\mathbf{V} ight]$	п	
1 ^H	-1.00; rev.	1	-1.16; rev.	1	
$1^{\rm H} f$	-1.00; rev.	1	-1.77; rev.	1	
2 ^{Me}	-1.17; quasi-irrev.	1 ^[b]	-1.17; quasi-irrev.	1 ^{[b}	
$2^{Me}f$	$-1.04 (E_{\rm pc})$; irrev.	1 ^[c]	-1.75; irrev.	1 ^{[c}	

[a] $E_{\frac{1}{2}}$ (vs. SCE) is calculated as $(E_{pa} + E_{pc})/2$ in which E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively, measured by cyclic voltammetry at 0.1 Vs⁻¹. *n* is the number of electrons involved in the redox process. [b] Determined with respect to the monoelectronic oxidation of ferrocene (Fc) in the reference complex **Fc-ph-2^{Me}** (Figure 5). The electrophore^{+/0} cathodic wave merges with the electrophore^{0/-} (bi-electronic 1+1 electron unresolved wave). [c] For determination of this *n* value, see the text.

The number of electrons (n) involved in the various redox processes was essentially derived from the electrochemical study of the corresponding inorganic dyads made up of a covalently linked coordination compound (as the one-electron

oxidizable internal reference) and the pyridinium moiety under consideration. Typically, Ru^{II} and Os^{II} bis-terpyridine complexes were used for the $\mathbf{1}^{\mathbf{H}[9,38]}$ and $\mathbf{1}^{\mathbf{H}} f$ electrophores (Figure S-XXIIIa-c in the Supporting Information) and ferrocenyl-based dyads (Figure 5), specifically synthesized for the purpose, were used for the hexa-branched tetraand methyl-substituted electrophores 1^{Me} and 2^{Me} . Rotating disc electrode experiments unambiguously showed that two electrons are involved in the quasi-irreversible reduction process of 2^{Me} , whereas the two reduction processes observed at -1.00 and -1.16 V were confirmed as monoelectronic in the case of 1^{Me} (Figure 5). With regard to $2^{Me}f$, its electrochemical behavior was found to parallel that of $\mathbf{1}^{H} f$ (except for the reversibility), as judged from a comparison of the outcomes of cyclic voltammetry (see Table 1 and the Supporting Information). Indeed, two successive reduction processes occur at roughly the same potentials (ca. -1 and -1.75 V, Table 1) in the two fused species $1^{H}f$ and $2^{Me}f$ whereas the two monoelectronic reductions of the parent branched precursors 1^{H} and 2^{Me} more or less merge at around -1 V. On the basis of the analogous electrochemical behavior of the two couples $(1^{R2}/1^{R2}f)$ and $(2^{R2}/2^{R2}f)$, it is inferred that the two reduction processes recorded for $2^{Me}f$ are most likely monoelectronic (Table 1). The number of electrons (n=1) was confirmed by using data from the rotating disc electrode voltammograms and their logarithmic treatments, assuming that the reduction process is governed by the Nernst equation.^[70]

With respect to the different degrees of electrochemical reversibility observed for the first reduction process(es) of various species, one should make a basic distinction between the behavior of branched and pericondensed electrophores.

Regarding the branched species, distinct electrochemical reversibilities are observed depending on whether the pyridinium core is tetra-branched 1^{R2} (**TP**⁺ type, see Scheme 1) or hexa-branched 2^{R2} (**XP**⁺ type, see Scheme 2), as illustrated in Figure 5. The only significant difference between these two types of molecules resides in the level of steric encumbrance at the periphery of the electroactive pyridinium core. In fact, the two monoelectron reductions are energetically



Figure 5. Determining the number of electrons (*n*) involved in the first reduction processes of branched pyridiniums and assessing the related electrochemical reversibilities. Left) Dyad **Fc-ph-1**^{Me} ($c=2.5 \times 10^{-4}$ M): a) Cyclic voltammetry ($\nu=0.1$ Vs⁻¹) and b) rotating disc electrode voltammetry ($\nu=0.01$ Vs⁻¹; rotation rate: 2×10^3 rpm). Right) Dyad **Fc-ph-2**^{Me} ($c=2.8 \times 10^{-4}$ M): c) Cyclic voltammetry ($\nu=0.1$ Vs⁻¹) and d) rotating disc electrode voltammetry ($\nu=0.1$ Vs⁻¹) and d) rotating disc electrode voltammetry ($\nu=0.1$ Vs⁻¹) and d) rotating disc electrode voltammetry ($\nu=0.1$ Vs⁻¹) and d) rotating disc electrode voltammetry ($\nu=0.1$ Vs⁻¹).

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equally demanding in both cases (occurring at ca. -1 V), but only in the case of $[XP]^-$ is back transformation (reoxidation) to the starting native \mathbf{XP}^+ impeded. Changing the scan rate [range: 0.025-1 Vs⁻¹] impacts sizably on the degree of irreversibility of the process: Reoxidation is found to be more effective at high scan rate. As far as we know, no coupled chemical reaction is expected to occur for the **XP⁺** molecule subsequent to reduction. Given that the reoxidation process requires the retrieval of electrons from the reduced pyridinium core, its shielding by the six pendant aryl groups through a probable structural reorganization might hinder its accessibility to the electrode surface. Therefore a huge structural reorganization resulting from the rearrangement of bonds within the reduced pyridinium could be the limiting factor partly circumvented when the scan rate is high. To clarify the nature of the possible redox-induced structural distortion of the molecular backbone of $[2^{Me}]^{-}$, ab initio calculations were undertaken. Structural optimization was carried out in the absence of constraints and by taking into account solvent effects (namely acetonitrile) for the hexa-branched molecule in its native monocationic $[2^{H}]^{+}$, neutral monoreduced, [2^H]⁰, and negatively charged twoelectron reduced $[2^H]^-$ states. It was found that the propeller-shaped geometry is retained for the one-electron-reduced species. The structural relaxation is apparent in the

overall flattening of the molecular backbone resulting from the planarization of the branches with respect to the pyridinium core (the interannular twist angles decrease on average from 70.4 to 65.9° upon reduction).^[71] Addition of a second electron induces a dramatic boat-shaped distortion of the pyridinium core correlated with pyramidalization of its nitrogen atom (see Figure 6). This distorted conformation is calculated to be more stable than that of the bi-reduced species frozen in the flattened propeller-shaped geometry by around 1.43 eV (33.06 kcalmol⁻¹). This unexpected skeletal distortion accounts for the lack of reversibility observed for the reduction of 2^{Me} .

On the other hand, the difference in the electrochemical reversibility noted for the first reduction of the expanded pyridiniums $1^{H}f$ and $2^{Me}f$ is instead ascribed to differences in the hindrance experienced by the carbon atom *para* to the N_{pyridinio} atom (that is, the 4-position of the pyridinium motif A, noted A4 in Figure 4 (inset); see also the Supporting Information). Thus, when exposed, the site A4 (and to a lesser extent the sites A2 and A6), with its recognized peculiar (chemical) reactivity,^[37] is potentially subject to nucleophilic attack (pseudobase reactivity yielding addition products),^[40,72–75] reductive dimerization,^[17b,76] or pimerization.^[69b] Appending bulky substituents capable of hindering the approach of a potential reactant at the site A4 is a widely used



Figure 6. Computed geometries for a) native $[2^{H}]^{+}$, b) flattened monoreduced $[2^{H}]^{0}$, and c) top and d) side views of the distorted bi-reduced $[2^{H}]^{-}$.

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strategy for overcoming these detrimental effects. Aryl groups are typically used for these protective substituents,^[77,78] as illustrated by the reversible first reduction of 1^{H} ; bare *N*-methylpyridinium as a reference shows an irreversible reduction.^[17] This behavior is also reminiscent of that of acridinium: Its reduction is normally an irreversible process,^[79,80] which becomes reversible for the *N*-methyl-9-phenylacridinium^[80b] bearing a pendant phenyl group at the A4 position of the central pyridinium motif, as expected.^[81] Thus, simple inspection of the molecular structures (Schemes 1 and 2) allows us to infer that, amongst the fused species studied, $2^{Me}f$ should be the most prone to undergo such a chemical reaction, as experimentally verified (Table 1).

Note here that accounting for the electrochemical properties of the whole series of electrophores, whether "branched" or "fused" (including acridinium derivatives), basically involves a discussion of the properties of the pyridinium motif as the key electroactive fragment. When comparing the electron-accepting abilities of "branched" and "fused" expanded pyridiniums, it is found that their first reduction potential does not substantially change upon pericondensation of the branched molecular scaffold. More precisely, these reduction potentials do not become more positive (anodic shift) when the "core aromatic ring system becomes larger", as in the case of the benchmark perylene diimide family.^[35,36] The first reduction potential of all four $1^{\rm H}$, $1^{H}f$, 2^{Me} , and $2^{Me}f$ electron acceptors lies at roughly -1 V (vs. SCE). Differences between the "branched" and "pericondensed" pyridiniums emerge for the second reduction process. This second monoelectronic reduction occurs at a potential very close to the first monoelectronic reduction for both "branched" species (within ca. 0.2 V, see Table 1), whereas it occurs at a significantly higher potential for "fused" species (at ca. -1.75 V vs. SCE for both $1^{H}f$ and $2^{Me}f$). This finding strongly suggests that, contrary to the first reduction, the active molecular orbitals (MOs) should show a pronounced delocalized nature. In other words, for the first reduction process, extending the π system does not lead to an enhancement of the π delocalization, whereas it does for the second reduction. Ongoing theoretical investigations will tell us whether the primary dominant pattern of the pyridinium (electronic) entity is lost after the first reduction.

Expanded pyridiniums as chromophores and luminophores—insights into the electronic features of the ground and excited states: Pyridiniums are usually considered for their electron-withdrawing and -accepting properties but rarely for their electronic or photophysical properties. We examine here the extent to which pericondensation can provide pyridiniums with appealing chromophoric and luminophoric features likely to renew their interest and use.

Electronic absorption spectra: The absorption spectra of the branched and corresponding fused chromophores are given in Figure 7 and the data are collected in Table 2.

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Figure 7. Typical electronic spectra of the native and fused derivatives (acetonitrile solutions). Top) Native $[1^{H}](BF_{4})$ (dotted) and fused $[1^{H}f](BF_{4})$ (solid). Bottom) Branched native $[2^{Me}](BF_{4})$ (dotted) and fused $[2^{Me}f](BF_{4})$ (solid).

The native and fused derivatives exhibit significantly different electronic properties. The $[\mathbf{R}^0 ph - \mathbf{TPR}^1_2 \mathbf{R}^2]^+$ branched acceptors (see Scheme 1) usually display only one main absorption band at about 310 nm^[10a, 38] whereas the corresponding fused acceptors have much more complicated features^[39b,72] that moreover extend towards the visible domain $(1^{H}f$ is bright yellow whereas 1^{H} is colorless). Of note, also, is the marked increase in the molar extinction coefficients of the absorption bands upon pericondensation. The same trend is observed on going from the hexa-branched 2^{Me} (displaying an ill-defined and featureless absorption spectrum) to the hemifused $2^{Me}f$ (Figure 7). With regard to the absorption spectrum of branched species of the XP^+ type, it is worth noting not only the absence of the strong absorption band at around 310 nm, but also the fact that the two chromophores (TP⁺ and XP⁺) show similar integrated absorptions in the investigated spectral window whereas one could reasonably expect a significantly larger integrated absorption for the hexaaryl chromophore (XP+ type) compared with the tetraphenyl one (TP⁺ type). This observation can be explained as follows: Previous detailed studies of the electronic properties of **TP**⁺-like chromophores showed that the strong absorption at around 310 nm is basically chargetransfer (CT) in nature,^[42] comprising two π - π * intramolecular CT components between the electron-donating periph-

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Table 2. Electronic absorption data for expanded pyridiniums (branched and pericondensed).^[a]

$\lambda_{ m max} \left[{ m nm} ight] \left(arepsilon \left[{ m 10^4} { m m^{-1}} { m cm^{-1}} ight] ight)$										
1 ^н		242.5sh		308.5						
		(1.40)		(3.83)						
$1^{\rm H} f$	226.5 (5.12)	239.0sh	278.5sh	302.0	327.0sh	348.0	359.0sh	383.0sh	407.5	429.0
		(4.54)	(4.13)	(6.78)	(2.28)	(2.41)	(2.00)	(0.40)	(0.82)	(1.00)
2 ^{Me}	222.5sh (5.19)	258.0		304.0		340.5sh				
		(1.88)		(1.10)		(0.67)				
$2^{Me}f$	227.0 (8.46)	264.5	280.5	317.0			352.0sh	370.0sh	402.5	423.5
		(3.57)	(3.37)	(4.44)			(1.27)	(0.73)	(0.71)	(0.98)

[a] Acetonitrile solutions; sh: shoulder; band maxima are given as a function of their energy, not on the basis of their hypothetical nature or affiliation.

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solution at room temperature (RT) and in a butyronitrile rigid matrix at 77 K (low temperature, LT; see Table 3 and Figure 8).

Because of the energies of the excited states, the lifetimes, the room-temperature quantum yields, and the spectral shapes, the luminescent properties (fluorescence at room temperature, both fluorescence and phosphorescence at 77 K) are

attributed to excited states with a dominant $\pi - \pi^*$ nature.^[84]

eral 2,6-aryls and the 4-aryl on the one hand, and the pyridinium core on the other.^[82] Therefore, on passing from **TP**⁺ to the burdened propeller-shaped **XP**⁺ chromophore in which enforced askew-stacked aryl rings are tilted almost perpendicularly out of the plane of the central pyridinium platform, it is expected that both the molar absorptivity and the energy of the merged intramolecular CT bands will be heavily affected. This is indeed the case. Similar changes have been reported for the electronic absorption of the two rotamers of the *N*-methyl-2,4,6-triphenylpyridinium salt, the phenyls at the 2,6 positions being conformationally locked almost coplanar or perpendicular to the pyridinium ring: On going from the former to the latter, the absorbance of the CT band is significantly reduced and also blueshifted (ca. 1500 cm^{-1}).^[82b]

With respect to the fused species, a salient feature shared by $1^{H}f$ and $2^{Me}f$ is the two-band pattern present at the red edge of their absorption spectra, which is also found in the spectra of other members of the family.^[39b] The energy difference between these two bands remains virtually the same for both $1^{H}f$ and $2^{Me}f$ (ca. 0.152 eV/1230 cm⁻¹) as well as for all the [R^{0} - $fTPR^{1}_{2}$ -ph R^{2}]⁺ class of chromophores^[39b] regardless of the nature of the solvent, hence the inference of a pronounced vibronic contribution. Such a vibronic effect has already been characterized in the case of $1^{H}f^{[83]}$ and is also confirmed at the photophysical level.

Thus, the impact on the electronic features of pyridiniums that we observe upon pericondensation is as follows: On going from the branched to the pericondensed pyridiniums, there is a marked increase in both the number of absorption bands around the red edge of their electronic absorption spectra and their extinction coefficients. These observations are indicative of a densification of molecular orbitals (MOs) around the HOMO–LUMO gap, which is also reduced. Given that electrochemistry tells us that the energy of the LUMO remains virtually unchanged upon ring fusion (the first reduction potential is the same in corresponding branched and fused pyridiniums), the reduction of the HOMO–LUMO gap should result from an increased energy of the HOMO within pericondensed chromophores relative to the branched parents.

Luminescence properties: All the expanded pyridiniums investigated here are photoluminescent, both in acetonitrile

Comparison of the branched and pericondensed expanded pyridiniums: With respect to the fluorescence emission at

Table 3. Photophysical properties (Fl.: fluorescence; Ph.: phosphorescence; λ/nm) of the luminophores at both room temperature (RT) in deoxygenated acetonitrile fluid solution and 77 K (LT) in a butyronitrile rigid matrix.^[a]

Entry	Luminescence, RT					Luminescence, LT			
	λ _{Fl} [nm]	$arPsi_{ m Fl}$	$ au_{ m Fl}$ [ns]	$k_{ m r} [{ m s}^{-1}]$	$k_{ m nr}$ [s ⁻¹]	λ _{Fl} [nm]	$\tau_{\rm Fl}$ [ns]	$\lambda_{\rm Ph}$ [nm]	$ au_{ m Ph}$ [ms]
1 ^{H[b]}	480	$< 10^{-4}$	3.0	$< 3.33 \times 10^{4}$	$> 3.33 \times 10^{8}$	390	5.1	450	107
$1^{\rm H} f$	465	0.35	7.0	5.00×10^{7}	9.28×10^{7}	439	10.0	494	4500
2 ^{Me}	455	0.48	8.0	6.00×10^{7}	6.50×10^{7}	395	5.0	455	2500
2 ^{Me} f	479	0.13	6.7	1.94×10^{7}	1.30×10^{8}	430	7.7	498	3945

[a] No phosphorescence emission was detected at room temperature for any of the species. [b] From ref. [38].

room temperature, the values of the Stokes' shifts (SS) are very different depending on the degree of fusion in the molecular scaffolds, the largest (and even in the range of unusually large Stokes' shifts, 5000-15000 cm⁻¹)^[85] being for the branched luminophores and especially for the less crowded of them, that is, $\mathbf{1}^{H}$ (SS = 11580 cm⁻¹, which compares with ca. 7390 cm⁻¹ for 2^{Me}), as expected. The excitedstate structural relaxation responsible for this phenomenon is planarization,[86] which involves aryl rings connected at both the $2,6+4^{[82]}$ and the N^[42,87] pyridinio positions. Thus, upon photoinduced excitation, the whole molecular backbone flattens according to adiabatic torsional motions around interannular bonds.^[42,82,87] Regarding the SS values of the pericondensed pyridiniums, which are small, they follow the expected trend with the larger value for the fused pyridinium bearing three pendant phenyl rings $(2^{Me}f: SS)$ \approx 2740 cm⁻¹) and the smaller for the single phenyl-substituted pyridinium ($\mathbf{1}^{\mathbf{H}} \mathbf{f}$: SS \approx 1800 cm⁻¹).

Insights into the deactivation pathway(s) can also be gained from the analysis of the variation of the blueshifts (BS) of the fluorescence emission energy observed on passing from room-temperature fluid solutions to low-temperature rigid matrices. The blueshift reflects the energy destabilization of the (emissive) lowest-lying singlet state when solvent reorganization, which normally accompanies excitedstate intramolecular charge redistribution and subsequent



Figure 8. Luminescence spectra of $1^{H}f$ (top) and $2^{Me}f$ (bottom). The dotted spectra are room-temperature emission spectra in acetonitrile, the solid spectra are emission spectra recorded in butyronitrile at 77 K in the steady-state mode, and the dashed-dotted spectra are luminescence spectra recorded in butyronitrile at 77 K with a delay of 10 µs from excitation pulse (gate time 1 ms). In the latter case, fluorescence is suppressed and only phosphorescence is evidenced.

structure (here conformation) changes, is impeded (i.e., frozen). It is expected that the larger the intramolecular reorganization (reflected by Stokes' shifts) the larger should be the blueshift of the emission. In fact, this correlation is indeed observed because the same trends as for the Stokes' shifts are found: 1) For branched pyridiniums, the BS value for 1^{H} (BS=4810 cm⁻¹) is larger than that for 2^{Me} (BS=3340 cm⁻¹) and 2) for the pericondensed pyridiniums, the BS values are smaller than those of the related branched luminophores and moreover the BS value for 2^{Me} (BS=2380 cm⁻¹) is larger than that for $1^{\text{H}}f$ (BS=1270 cm⁻¹).

These observations are in line with changes in the emission quantum yields on passing from $1^{\rm H}$ to $1^{\rm H}f$, which suggests a contribution of intramolecular torsional motions to the nonradiative deactivation pathways of the equilibrated singlet excited state. However, structural relaxation is not the dominant factor as far as the luminescence properties are concerned in these compounds, as revealed by the analysis of the relative values of the radiative (k_r) and nonradiative $(k_{\rm nr})$ decay rate constants. Indeed, the $k_{\rm nr}$ rate constant decreases by a factor of 3.6 on going from $1^{\rm H}$ to $1^{\rm H}f$, whereas the emission quantum yield increases by more than three

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orders of magnitude (i.e., the k_r value of the fused species is 1.5×10^3 larger than that of the branched parent, see Table 3). It follows that despite their chemical parentage, these two luminophores are basically different in nature. In other words, from the viewpoint of their photophysical properties, there is no obvious parentage between the branched and chemically related pericondensed pyridiniums.^[88]

Comparing tetra- and hexa-branched expanded pyridiniums:

Of note is the intriguing photophysical behavior of the propeller-shaped pyridinium luminophore 2^{Me} . The connection between the 1^{H} and 2^{Me} expanded pyridiniums, whether considering the chemical, electrochemical (Table 1), electronic (Table 2), or photophysical (i.e., low-temperature fluorescence and phosphorescence emission energies in Table 3) properties, is not a matter of debate: They are both branched pyridiniums. However, it appears that k_{nr} is reduced by a factor of five (at least) on going from the tetrato the hexa-branched luminophore, whereas the related emission quantum yield is increased by a factor of 4.8×10^3 (i.e., the value of k_r for 2^{Me} is 1.8×10^3 larger than that of 1^{H} , see Table 3). This discrepancy can be explained as follows: The weak fluorescence of $\mathbf{1}^{H}$ at room temperature is ascribed to excited-state CT between the N-phenyl group and the pyridinium core.^[42,87,89] Although the two π systems are geometrically and electronically decoupled in the ground state,^[42] the CT in the excited-state is accompanied by a large torsional motion around the interannular C-N⁺ bond. As a consequence, the Franck-Condon factor for radiationless decay of the excited state increases accordingly, hence the nonradiatively short-circuited fluorescence emission. In 2^{Me} , on the other hand, not only is the overall molecular backbone greatly rigidified, but more importantly, planarization of the N-aryl group is largely hindered because of intramolecular steric crowding. Similarly to the impact of the enforced perpendicular layout of the determining 2,6-aryl rings on the electronic absorption properties, the steric constraining of the N-phenyl ring sharply out of the pyridinium plane heavily affects the energy of the excited-state CT, as reflected by the blueshifted room-temperature fluorescence emission (455 nm) relative to that of the more flexible tetrabranched 1^{H} (480 nm). This short-wavelength shift is also translated into a markedly reduced Franck-Condon factor, hence the dramatically improved emission of 2^{Me} .

Finally, the vibronic (fine) structures of $1^{H}f$ and $2^{Me}f$ identified in the electronic absorption spectra (Figure 7)^[83] are further substantiated by the structured emission spectra recorded at low temperature (Figure 8). The "two-band" pattern apparent in both the fluorescence and phosphorescence spectra of the compounds at 77 K is due to vibrational progressions but not to the different emissions, as is clearly demonstrated by the same lifetimes measured for these two vibronic bands. Moreover, the energy gaps between these two bands derived from low-temperature fluorescence emission ($1^{H}f$: ca. 1150 cm⁻¹; $2^{Me}f$: ca. 1175 cm⁻¹) correlate well with the energy gaps derived from the absorption spectra (1230 cm⁻¹, see above).^[90]

To summarize, the photophysical behavior of the pyridiniums as luminophores is greatly improved^[2] upon pericondensation of their molecular scaffolds by bis-cyclization. The extension of the π system with a correlative reduction of the HOMO-LUMO energy gap, already inferred from the electronic absorption properties, is further confirmed here by low-temperature fluorescence measurements. The fluorescence emission energy is indeed redshifted from 390-395 nm for the branched pyridiniums to 430-440 nm for the pericondensed ones. Beyond the positive impact^[2] on the luminescence of the increased overall molecular rigidity resulting from pericondensation, it is a matter of fact that the photobis-cyclization of branched pyridiniums gives rise to a basically new and different type of luminophore. Thus, poor luminophores like N-phenyl-substituted tetra-branched pyridiniums are transformed into good luminophores and thereby are in the top range of 0.1-1 for emission quantum yields. Also of interest is the peculiar case of the pyridinium 2^{Me} , which becomes highly fluorescent upon peraryl substitution, another valuable approach for expanding the pyridinium's scaffold.

General Comments

Photo-bis-cyclization: Photochemical cyclodehydrogenation is not driven to completion in the case of the hexa-branched pyridinium 2^{Me} , but stops after two cyclizations (that is, two C–C bond formations) to give the hemifused species $2^{Me}f$ as the major photoproduct. To account for this observation, one may invoke the following three points.

1) Even though photo-bis-cyclization can take place around the $N_{\text{pyridinio}}$ -aryl group, as demonstrated by the phototransformation of $\mathbf{1}^{\text{H}}$ into $\mathbf{1}^{\text{H}}f$, the opposite pyridinium site located *para* to the N_{pyridinio} atom is apparently favored when the pivotal ph-R² aryl is surrounded by two adjacent phenyls (R³=H), as in the case of $\mathbf{2}^{\text{R2}}$, irrespective of whether the R² substituent (Scheme 2) is a methyl group ($\mathbf{2}^{\text{Me}}$) or a simple proton ($\mathbf{2}^{\text{H}}$). In the latter case of selective hemifusion within the hexaphenylpyridinium, one can reasonably expect that the dissymmetry attached to the core pyridinium platform is most likely the basic origin of the differential reactivity of the various possible sites of photo-bis-cyclization, which are actually only two, with the one at the 4-position of the pyridinium preferred, other things being equal, that is, R⁰=R¹=R²=R³=H (Scheme 2).

2) Once the bis-cyclized and nicely luminophoric $[hfXPH_2R^2]^+$ fragment (see structure in Scheme 2) is formed around the branch *para* to the N_{pyridinio} atom, it behaves as a well in which the energy subsequently absorbed by the whole chromophore is funneled instead of being involved in the induction of further electrocyclic rearrangements required for further cyclizations. This scenario is in line with previous observations concerning the photochemistry of molecular assemblies made up of two **TP**⁺-like subunits covalently linked through a bridging spacer (of variable length) connected to the N_{pyridinio} position. In this case it has

been shown that ultrafast intramolecular singlet-singlet energy transfer occurred and affected the photochemical cyclodehydrogenation process so that once the first TP+-like moiety is transformed into the fused fTP^+ -like fragment, further photocyclization of the remaining TP+-like subsystem is inhibited.^[91] The photochemical behavior of photosensitizer-acceptor (P-A) inorganic dyads designed to undergo PET to form charge-separated states provides another illustration of inhibited photocyclization by competing energy transfer. For a decade now, we have been studying these dyads based on Ru^{II}/Os^{II} complexes of oligopyridines as the colored (abs. at ca. 500 nm) P component covalently linked to 2,4,6-triarylpyridinio groups (TP⁺) as the colorless (absorption in the UV) electron acceptor A and we never observed the formation of the bis-cyclized photoproduct *f***TP**⁺.^[38]

3) Further photocyclization processes are also likely to be impeded by the formation of sterically hindered high-energy intermediates that show detrimental structural constraints, as also observed in the case of chemical cyclization.^[92] In fact, the molecular backbone of $2^{Me}f$ exhibits a marked curvature of its fused part (Figure 3) indicative of intramolecular structure constraints, which might also appear as constrained torsional motions for the pendant phenyl rings at the 1-, 2-, and 6-positions (i.e., rings B and C; see nomenclature in the Supporting Information).

These three factors together can explain the selective biscyclization of the 2^{R^2} hexa-branched pyridinium solely into the $2^{R^2}f$ hemifused species ($R^2=H$, Me; see Scheme 2 for structural formulae), that is, without the formation of any other hemifused species or a mixture of different bis- or higher-cyclized products, including the fully pericondensed iminio analogue of hexa-*peri*-hexabenzocoronene.

The particular case of the propeller-shaped hexa-branched pyridinium: First, it is interesting to note that in spite of the respectable overall rigidity of the propeller-shaped molecular skeleton of 2^{Me} , large-amplitude structural rearrangements can take place upon the two-electron reduction of the electroactive pyridinium core (Figure 6). Such a large distortion is the result of the conflicting contributions of intramolecular steric hindrance and electronic factors associated with the necessary rearrangement of bonds (i.e., electronic relaxation) that accompanies bi-electronic reduction. Here, the positive side-effect of correlated (and even concerted)^[93] reduction processes and structural changes is the merging of the two separate monoelectronic reductions observed for tetra-branched species (see Figure 5) into a single bi-electronic process. So-called "potential inversion"^[94] is most likely responsible for this intriguing electrochemical behavior. We are currently investigating this phenomenon and exploring 1) the way the reduction potential of the bi-electronic process can be shifted towards more positive values and 2) the conditions by which the electrochemical reversibility of this two-electron process can be restored and even made switchable by monitoring the structure of the electrophore.

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Secondly, it is worth noting that, on the one hand, the nonluminescent bare *N*-methylpyridinium becomes fluorescent at room temperature upon aryl substitution (e.g., *N*-methyl-2,4,6-triphenylpyridinium), but that, on the other hand, replacing the $N_{pyridinio}$ -methyl group with an aryl group dramatically alters the emission properties, as exemplified by 1^{H} . Interestingly, bright luminescence is restored upon peraryl substitution of the pyridinium core (e.g., 2^{H} and 2^{Me}) as a result of the combined contributions of 1) geometry-related energy destabilization of the detrimental charge transfer from the *N*-aryl group to the pyridinium core and 2) the overall rigidification of the molecular backbone. Thus, there is an interest in expanding the pyridinium core not only by pericondensation but also by peraryl substitution to obtain pyridiniums that show good luminophoric features.

Conclusion

From a simple inspection of the molecular structures of pericondensed expanded pyridiniums, $\pi - \pi$ stacking in the solid state and aggregation in solution are naturally expected by analogy with their PAH counterparts. However, the picture we obtain from experimental cross studies, and in particular from solid-state X-ray crystallography and fluid solution NMR analyses, is that such interactions are not prominent and not even determining. Although not directly evidenced, coulombic repulsion between cationic pericondensed species could partly explain this finding, for instance, contributing to make the sharply different "head-to-head" and "tail-totail" cofacial layouts energetically comparable, hence the pseudopolymorphism observed for the tetrafluoroborate salt of bare $1^{H}f$. The features of the counteranion alone (e.g., size, shape) are not that determining for the columnar organization of pericondensed pyridiniums like $1^{H}f$ and other secondary interactions such as hydrophobic interactions seem preferable and even mandatory for the rational control of supramolecular assembly. As demonstrated by Müllen and co-workers, long alkyl chain(s), whether borne as decoration(s) by the pericondensed expanded pyridinium itself^[40,44] or provided by the associated counteranion,^[45] are indeed particularly efficient in this regard. Flat or curved (bowl-shaped)^[95] fused polycyclic pericondensed molecules are more appealing if they display additional features such as (cationic) charge and electroactivity and if the molecular properties can be tuned, including with respect to self-assembly. In fact, $1^{R2}f$ and $2^{R2}f$ (see Schemes 1 and 2) are versatile types of expanded pyridiniums that meet these criteria. On this basis they could serve, for instance, as new molecular building blocks of advanced multifunctional materials, including mesogens for discotic liquid crystalline materials,^[40,44,45,96] as novel molecular platforms in the emerging field of interfacial system chemistry,^[97] for (semi)rigid well-defined and shape-persistent organic dendrimers,^[98] or as smart molecules of pharmacological importance,^[99] following the example of the TOTA^[41] species as a model pharmacophore for DNA binding,^[100] among other potential applications.

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Another unexpected finding is the fact that extending the π -conjugated system to enhance π delocalization is not an efficient approach to ameliorate the electron-accepting ability of electrophores in the special case of pyridiniums, as reflected by the virtually unchanged value of the first reduction potential. The LUMO remains localized on the pyridinium core despite polycyclic ring fusion, that is, in spite of pericondensation. On the other hand, when the LUMO is not the only MO involved, the properties are markedly modified upon pericondensation. This is indeed the case for both the electronic absorption and, above all, the photoluminescence, as expected. These key issues allow derivation of the relevant guidelines for the future improvement^[2] of pyridiniums as multifaceted molecular objects of interest in their own right, following the example of benchmark perylene bisimide dyes,^[101] even though a strategy alternative to the extension of the π -conjugated system^[30,33,35,36] must be used to improve^[2] the electrochemical features. Typically, the well-established approach based on the synergistic close coupling of several pyridiniums will be applied to enhance the electron-accepting properties (anodic shift of reduction potentials). Such a strategy should also fruitfully apply to promising 2^{R^2} propeller-shaped hexaarylpyridiniums.

The whole aim is to obtain advanced expanded pyridiniums, that is, integrated multifunctional pericondensed and star-shaped branched bipyridiniums, which is the subject of ongoing work.

Experimental Section

Syntheses and characterization: Experimental procedures, characterization data for new compounds, and complete details for the synthesis of new compounds are available in the Supporting Information.

X-ray crystal structure determinations: Intensities were collected on a Bruker-Nonius Kappa CCD diffractometer ($Mo_{K\alpha}$, $\lambda = 0.71069$ Å, graphite monochromator) with sample-to-detector distances of 40 mm. The frames were integrated and corrected for Lorentzian and polarization effects using DENZO and the scaling and refinements of crystal parameters were performed by SCALEPACK. All structures were solved by direct methods (SIR97)^[102] and refined on F^2 with SHELXTL.^[103] Nonhydrogen atoms were refined anisotropically, hydrogen atoms were refined isotropically with a riding model except for [$\mathbf{1}^{H} \mathbf{f}$](BF₄) for which the non-methyl C–H distances were freely refined using SADI restraints ($\sigma = 0.03$).

CCDC-744709 ([$2^{Mc}f$](Cl)), -744710 ([$2^{Mc}f$](BF₄)), -744711 ([$2^{Mc}f$](FeCl₄)), and -744712 ([$1^{H}f$](BF₄)) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_ request/cif.

Crystal data for $[1^{H}f](BF_4)$: $[(C_{29}H_{18}N)^+, BF_4^-]$ -CH₃CN, M = 508.31, orthorhombic, *Pnna*, a = 7.263(2), b = 15.147(3), c = 21.543(4) Å, $\alpha = 90$, $\beta = 90$, $\gamma = 90^{\circ}$, V = 2370(1) Å³, Z = 4, $\rho_{calcd} = 1.425$ gcm⁻³, $\mu = 0.10$ mm⁻¹, T = 150 K, 18315 measured, 3767 independent, 2660 observed reflections ($\theta < 31.0^{\circ}$), R1 $[I > 2\sigma(I)] = 0.0614$, wR2 (all data) = 0.2008, S = 1.247 for 206 parameters and 28 restraints, residual electron density +0.43/-0.32 eÅ⁻³.

Crystal data for $[2^{M}f](BF_4)$: $[(C_{42}H_{28}N)^+, BF_4^-]$ -1.64H₂O, M=659.75, monoclinic, $P2_1/n$, a=19.648(3), b=8.320(2), c=20.745(4) Å, a=90, $\beta=97.96(3)$, $\gamma=90^{\circ}$, V=3358(1) Å³, Z=4, $\rho_{calcd}=1.303$ gcm⁻³, $\mu=0.09$ mm⁻¹, T=123 K, 32460 measured, 6253 independent, 4303 observed

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reflections ($\theta < 26.05^{\circ}$), $R1 [I > 2\sigma(I)] = 0.0609$, wR2 (all data) = 0.1464, S=1.17 for 486 parameters and 21 restraints, residual electron density +0.26/-0.22 eÅ⁻³. A two-fold orientational disorder was evidenced for two of the fluorine atoms of the BF₄ anion, the population coefficients refine to 0.50/0.50 and 0.60/0.40, respectively. A strongly disordered solvent region was found by Fourier synthesis, which, given the crystal growth conditions (only small needles could be obtained from MeOH/ H₂O), was attributed to water molecules of variable occupancy. These molecules were refined using constrained atomic displacement parameters.

Crystal data for [2^{Me}f](FeCl₄): [(C₄₂H₂₈N)⁺, (Fe^{III}Cl₄)⁻], M=659.75, monoclinic, $P2_1/c$, a=16.511(3), b=12.521(2), c=16.984(3) Å, a=90, $\beta=$ 95.56(3), $\gamma = 90^{\circ}$, V = 3494(1) Å³, Z = 4, $\rho_{calcd} = 1.415$ g cm⁻³, $\mu =$ 0.77 mm⁻¹, T=123 K, 54242 measured, 9001 independent, 6773 observed reflections ($\theta < 28.72^{\circ}$), R1 [$I > 2\sigma(I)$] = 0.0478, wR2 (all data) = 0.1446, S=1.18 for 434 parameters, residual electron density $+0.58/-0.38 \text{ e}\text{ Å}^{-3}$. Crystal data for $[2^{Me}f](Cl)$: $2[(C_{42}H_{28}N)^+, Cl^-]\cdot 2(H_2O)\cdot 0.75(CH_3OH),$ M = 1219.23, monoclinic, $P2_1/n$, a = 15.650(3), b = 16.078(3), c = 16.078(3)25.796(5) Å, $\alpha = 90$, $\beta = 106.43(3)$, $\gamma = 90^{\circ}$, V = 6226(2) Å³, Z = 4, $\rho_{calcd} =$ 1.301 g cm⁻³, $\mu = 0.16$ mm⁻¹, T = 123 K, 90121 measured, 12866 independent, 4303 observed reflections ($\theta < 26.5^{\circ}$), R1 [$I > 2\sigma(I)$]=0.1008, wR2 (all data) = 0.2497, S = 1.00 for 834 parameters and 646 restraints, residual electron density $+0.52/-0.30 \text{ e} \text{ Å}^{-3}$. In spite of their well-shaped morphology and their acceptable dimensions, the crystals are rather poorly diffracting. It might be that the beam damages them because attempts to collect data at room temperature were not successful. Owing to the lack of observed data, similarity displacement parameters restraints were applied to the ligand (σ =0.03), atomic displacement parameters constraints and bond length restraints (σ =0.03) were applied to the carbon and oxygen methanol solvent, and isotropic displacement parameters restraints were applied to the disordered water molecules ($\sigma = 0.02$).

Electrochemical measurements: The electrochemical experiments were carried out with a conventional three-electrode cell (solution volume of 15 mL) and a PC-controlled potentiostat/galvanostat (Princeton Applied Research Inc. model 263 A). The working electrode was a platinum electrode from Radiometer-Tacussel with an exposed geometrical area of 0.034 cm² and mounted in Teflon[®]. The electrode was polished before each experiment with 3 and 0.3 µm alumina pastes followed by extensive rinsing with ultra-pure Milli-Q water. Platinum wire was used as the counter-electrode and a saturated calomel electrode (SCE) as the reference electrode. Electrolytic solutions, acetonitrile (Aldrich, anhydrous, 99.8%) containing $0.1\,M$ tetrabutylammonium hexafluorophosphate (TBAPF₆, Aldrich, +99%) as supporting electrolyte were routinely deoxygenated by argon-bubbling. All the potential values are given versus SCE. The reported numerical values (Table 1) were corrected by using a Fc) equal to +0.380 V vs SCE in MeCN.^[104] Cyclic voltammetry experiments were conducted at a scan rate of 0.1 Vs⁻¹ (except where specified in the text). Rotating disc electrode voltammetry experiments were conducted at a scan rate of 0.01 Vs⁻¹ by rotating the disk electrode at 2000 rpm (Controvit device from Radiometer-Tacussel, France). Square wave voltammetry experiments were performed with a potential sweep rate of 100 mV s^{-1} (pulse height = 25 mV, step height = 2 mV, and frequency = 50 Hz).

Photophysical properties: For steady-state luminescence measurements, a Jobin Yvon-Spex Fluoromax 2 spectrofluorimeter was used equipped with a Hamamatsu R3896 photomultiplier, and the spectra were corrected for photomultiplier response using a program purchased with the fluorimeter. For the luminescence lifetimes, an Edinburgh OB 900 time-correlated single-photon-counting spectrometer was used in the ns range. A Hamamatsu PLP 2 laser diode (59 ps pulse width at 408 nm) and nitrogen discharge (pulse width, 2 ns at 337 nm) were employed as excitation sources. Emission quantum yields for argon-degassed acetonitrile solutions of the organic species were determined by using the optically diluted method^[105] with anthracene in air-equilibrated ethanol solution ($\Phi_{\rm em} = 0.2$) as the quantum yield standard.^[106]

 $\label{eq:computational details: All Calculations were carried out using a development version of the Gaussian code.^{[107]} A hybrid Hartree–Fock/density$

functional model, referred to as PBE0, was used,^[108] which was obtained by casting the PBE exchange and correlation functional^[109] in a hybrid HF/DFT scheme, in which the HF/DFT exchange ratio is fixed a priori to 1:3. The molecular structure of each compound was fully optimized and the nature of each stationary point was defined by a subsequent frequency calculation. All atoms were described by a double ζ quality basis set,^[110] Solvent effects were taken into account in all calculations by applying an implicit solvation model, that is, the polarizable continuum model (PCM) perfected by Tomasi and co-workers.^[111] More specifically, we used the conductor-like PCM model as implemented in the Gaussian development version Revision G.01,^[112] Acetonitrile was considered as solvent.

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