Highlight on the solution processes occurring on silver(I)-assembling porphyrins in presence of an excess of silver salt

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Coordination cages obtained upon complexation of pyridyl functionalized porphyrins by Ag⁺, disassemble when overtaking a 1:2 stoichiometric amount of silver salt. An excess of Ag⁺ then leads to unusual chemical processes, here analyzed in details, which permanently transform the monomeric porphyrins. The observed processes, discussed with reference to model compounds devoid of polyether substituted pyridyl residues, evidence a peculiar reactivity for *meso* 2,6-dimethylphenyl substituted porphyrins.

Introduction

Self-assembling multitopic ligands with metal ions is a simple and efficient process to obtain three-dimensional metallocupramolecular structures of high diversity.^{1–11} Coordination cage-type structures incorporating porphyrins are of high interest thanks to the ability of the large aromatic porphyrin core to interact with guest molecules *via* π -interactions and coordination bonds in the case of metallocupporphyrins.^{12–28} Such coordination containers have shown their potential as functional systems for molecular recognition,¹⁰ drug delivery²⁹ or as nanoreactors.^{5, 30, 31} Silver(I) ion, a kinetically labile diamagnetic metal ion with a versatile coordination sphere, is appealing for a two-component metal ligand process under thermodynamic control.^{12, 32–34} It can be engaged as a “naked” metal cation from numerous existing silver salts with solubility ranging from organic to aqueous solvents. Nevertheless, selective formation of the desired discrete coordination structures, as well as their stabilities regarding assembly and disassembly processes in presence of the metal ion, is crucial regarding the potential applications of the hollow structures.

We previously described the complexation of pyridyl functionalized porphyrins (**2H-TPyP** and **Zn-TPyP**)³⁵ by Ag⁺, as a useful tool to build self-assembled porphyrinic cages (Scheme 1).³² By means of NMR, high-resolution mass spectrometry and absorption and emission spectroscopy, we identified the

Scheme 1. Chemical structures of **2H-TPyP** and **Zn-TPyP** and respective models **2H-Ref** and **Zn-Ref**. The silver(I) coordination complexes **[Ag₄(2H-TPyP)₂]⁴⁺** and **[Ag₄(Zn-TPyP)₂]⁴⁺** are also shown.

quantitative formation of the coordination cages **[Ag₄(2H-TPyP)₂]⁴⁺** and **[Ag₄(Zn-TPyP)₂]⁴⁺** upon addition of two equivalents of Ag⁺. Detailed optical investigations, performed in CH₂Cl₂ dilute solutions, evidenced a reverse process of cage opening upon further addition of Ag⁺ up to four equivalents. More complex and altering processes occurred when exceeding the four equivalents of added ion. They will be analyzed and discussed in details here.

Results and discussion

Addition of increasing amounts of Ag⁺ to **2H-TPyP** (1.1 × 10^{−5} M) in the range 4–150 equivalents produces absorption changes shown in Figure 1. Two distinct families of curves can be identified: a first one (4–15 equivalents) with isosbestic points at 424, 469, 526 and 641 nm (Fig. 1a) and a second one

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Fig. 1. Absorption spectra of a solution of **2H-TPyP** in CH_2Cl_2 (1.1×10^{-5} M) upon addition of $[\text{Ag}(\text{SbF}_6)]$: a) $[\text{Ag}^+] = 4.3 - 15.0$ equiv; b) $[\text{Ag}^+] = 15.0 - 148.0$ equiv. Spectral changes in the Soret region (0.2 cm optical path) are reported in the insets.

(15-150 equivalents) characterized by isosbistics at 350, 428, 487 and 563 nm (Fig. 1b). As a general trend, the Soret band at 419 nm disappears while a new band shows up at 433 nm and a reduction in the number of Q-bands, from four to two new bands at 577 and 625 nm, occurs.

Similarly, emission spectra undergo important spectral changes upon addition of 4-15 equivalents of Ag^+ (Fig. 2). A blue-shift of the emission bands is observed with clear isosbistics at 639 and 697 nm. The quantum yield of the final emission is estimated to be 80% that of the initial **2H-TPyP**,³² i.e. 0.076. Further addition of Ag^+ equivalents, up to 150, do not produce any sizeable change. Excitation spectra confirmed that the final emission features originate from the species formed upon titration (Fig. S16). The measured lifetime of this species is 3.7 ns, shorter than that of the initial **2H-TPyP** (10.6 ns).³²

The absorption and emission features of the produced species resemble those reported for $\text{Ag}(\text{I})_2$ -porphyrin dinuclear complexes (a tentative representation is given in scheme 2).^{36, 37, 38} In particular, the location of the Q-bands in the 580-650 nm region supports this assignment. The biphasic behavior of the absorption titration can be ascribed to the stepwise approach of the $\text{Ag}(\text{I})$ ion to the two sides of the porphyrinic plane. We have no evidence of further disproportionation to a $\text{Ag}(\text{II})$ -porphyrin form, a process which is usually reported for

Fig. 2. Emission spectra of a solution of **2H-TPyP** in CH_2Cl_2 (1.1×10^{-5} M) upon addition of $[\text{Ag}(\text{SbF}_6)]$: $[\text{Ag}^+] = 4.3 - 15.0$ equiv. $\lambda_{\text{exc}} = 528$ nm.†

$\text{Ag}(\text{I})_2$ -porphyrins, leading to a main Q-band at ca. 540 nm and a blue-shifted and extremely weak emission.^{36, 37, 39} This process is ascribed to the large size of the $\text{Ag}(\text{I})$ ions that leads to a distorted and labile $\text{Ag}(\text{I})_2$ -porphyrin complex; the two $\text{Ag}(\text{I})$ ions of the complex easily disproportionate to generate a $\text{Ag}(\text{0})$ - $\text{Ag}(\text{II})$ couple where the smaller $\text{Ag}(\text{II})$ ion is readily accommodated into the porphyrin macrocycle.⁴⁰ Stabilization of the $\text{Ag}(\text{I})_2$ -porphyrin complex in this case can be due to the specific properties of the porphyrinic compound or to steric constraints caused by the *meso*-aryl substituents (see discussion below), allowing the characterization of the emission features of this complex which, to the best of our knowledge, has never been reported before in the literature.

Analogous titration studies have been performed for **Zn-TPyP**. Absorption changes observed upon addition of Ag^+ from 4 to 15 equivalents are reported in Fig. 3. A single equilibrium is observed with isosbestic points at 317, 414.5, 438, 530, and 564 nm. A pronounced blue-shift of the Soret band, from 422 nm to 410 nm, occurs together with the disappearance of the Q-bands and the growth of a broad absorption in the 600-800 nm region that extends in the NIR (see Fig. S17). The emission behavior is characterized by a progressive quenching of the fluorescence of the Zn-porphyrin, as reported in Fig. 4, indicating that the resulting species is non-emissive. The lifetime of the weak emission measured at the end of the titration is 2.2 ns, coincident with the lifetime of **Zn-TPyP**³² and ascribed to the small fraction of unquenched pristine porphyrin.

Scheme 2. Representation of $\text{Ag}(\text{I})_2$ -TPyP.

Fig. 3. Absorption spectra of a solution of **Zn-TPyP** in CH_2Cl_2 (1.1×10^{-5} M) upon addition of $[\text{Ag}(\text{SbF}_6)]$: $[\text{Ag}^+] = 4.0 - 15.2$ equiv. Spectral changes in the Soret region (0.2 cm optical path) are reported in the inset.

Fig. 4. Emission spectra of a solution of **Zn-TPyP** in CH_2Cl_2 (1.1×10^{-5} M) upon addition of $[\text{Ag}(\text{SbF}_6)]$: $[\text{Ag}^+] = 4.0 - 15.2$ equiv. $\lambda_{\text{exc}} = 530$ nm.

The observed absorption features closely resemble those detected upon electrochemical oxidation of Zn-porphyrins^{41,42} leading to the radical cation $\text{ZnP}^{+\cdot}$ and are undoubtedly indicative of a process of oxidation of the porphyrin macrocycle. Oxidation of Zn-porphyrins by $\text{Ag}(\text{I})$ has been proposed as reaction mechanism in the synthesis of *meso-meso* linked multiporphyrin arrays: the $\text{Ag}(\text{I})$ promoted oxidative coupling is thought to proceed through the formation of an intermediate porphyrin radical cation.^{43, 44} Relatively stable Zn-porphyrin radical cations in solutions have been reported only upon electrochemical generation or pulse radiolysis in presence of strong oxidants.⁴⁵ The formation of a stable radical cation for **Zn-TPyP** with the addition of 15 equivalents of a generally mild oxidant as $\text{Ag}(\text{I})$ seems to be related to the peculiar chemical properties of the porphyrin compound and/or the $\text{Ag}(\text{I})$ ions in the present experimental conditions. The occurrence of these processes allowed to find out that the produced Zn-porphyrin radical cation is non-emissive in the explored spectral range.

In order to ascertain if the observed processes could be promoted by the appended polyether substituted pyridyl residues in **2H-TPyP** and **Zn-TPyP**, the same titration

experiments have been performed with model compounds (**2H-Ref** and **Zn-Ref**, Scheme 1) where the polyether substituted pyridyl residues are replaced by methoxy and triflate groups, respectively. In the 0–2 equivalents range no spectroscopic changes consistent with those observed for **2H-TPyP** and **Zn-TPyP** were detected, confirming that in this interval the features observed for the pyridyl substituted porphyrins originate from the formation of the coordination cages.³² Upon addition of Ag^+ , both **2H-Ref** and **Zn-Ref** undergo solely spectral changes similar to those detected for **2H-TPyP** and **Zn-TPyP**, respectively, when exceeding four equivalents. These processes are described in details below.

Absorption titration of **2H-Ref** in the range 0–150 equivalents results in two equilibria, with a final red-shift of the Soret band from 416 to 424 nm and a reduction of the four Q-bands into two bands at 573 and 621 nm (Fig 5). Emission spectra show a hypsochromic shift from the original maxima at 654 and 716 nm to 634 and 688 nm (Fig 6). Excitation spectra collected at 630 and 690 nm allowed to ascribe the final emission to the species formed upon titration (Fig. S18). Its emission quantum yield is 90% that of the initial **2H-Ref**, i.e. 0.10 (Table S11). The lifetime of the new species is 4.7 ns, shorter than that of **2H-**

Fig. 5. Absorption spectra of a solution of **2H-Ref** in CH_2Cl_2 (1.1×10^{-5} M) upon addition of $[\text{Ag}(\text{SbF}_6)]$: a) $[\text{Ag}^+] = 0 - 16.4$ equiv (isosbestic at 337, 379, 423.5, 463, 526, 593, 607, 642 nm); b) $[\text{Ag}^+] = 16.4 - 150.0$ equiv (isosbestic at 261 and 420 nm). Spectral changes in the Soret region (0.2 cm optical path) are reported in the insets.

Fig. 6. Emission spectra of a solution of **2H-Ref** in CH_2Cl_2 (1.1×10^{-5} M) upon addition of $[\text{Ag}(\text{SbF}_6)]$: $[\text{Ag}^+] = 0 - 150.0$ equiv. $\lambda_{\text{exc}} = 528$ nm. Isosbestic at 644 and 700 nm.

Ref (10.2 ns, Table S11). Analogously to **2H-TPyP**, we identify the formed species as the **Ag(I)₂-Ref** complex, whose emission properties (spectrum, emission quantum yield and lifetime) could be characterized.

Titration of **Zn-Ref** with $\text{Ag}(\text{SbF}_6)$ produces changes in the absorption spectra following a single equilibrium, with a hypsochromic shift of the Soret band from 421 to 411 nm and the formation of new bands at 674 and 926 nm, the latter extending in the NIR (Figs. 7, S19). In parallel, the addition of Ag^+ causes a complete quenching of the fluorescence of the Zn porphyrin (Fig. 8). As for **Zn-TPyP**, the observed changes are ascribed to a process of oxidation of **Zn-Ref** leading to a non-emissive porphyrin radical cation.

Fig. 7. Absorption spectra of a solution of **Zn-Ref** in CH_2Cl_2 (1.1×10^{-5} M) upon addition of $[\text{Ag}(\text{SbF}_6)]$: $[\text{Ag}^+] = 0 - 14.5$ equiv. Spectral changes in the Soret region (0.2 cm optical path) are reported in the inset.

The results indicate that the processes observed after the disruption of the coordination cages (Ag^+ exceeding four equivalents) do not strictly depend on the polyether substituted pyridyl residues of **2H-TPyP** and **Zn-TPyP** and take place similarly in the reference monomers. Their occurrence has to be related rather to common features in the structures of the four porphyrins, *i. e.* the four *meso* 2,6-dimethylphenyl substituents. Indeed, they could modify the redox

Fig. 8. Emission spectra of a solution of **Zn-Ref** in CH_2Cl_2 (1.1×10^{-5} M) upon addition of $[\text{Ag}(\text{SbF}_6)]$: $[\text{Ag}^+] = 0 - 14.5$ equiv. $\lambda_{\text{exc}} = 530$ nm.

properties of the porphyrins.^{46, 47} Moreover, they introduce some crowding on the porphyrin faces and steric constraints about the *meso*-aryl C-C rotation.^{35, 47-50}

In order to ascertain the role of the porphyrin redox potentials in the observed processes, an electrochemical characterization was performed on **2H-TPyP**, **Zn-TPyP**, the two models **2H-Ref** and **Zn-Ref**, and two archetypal reference compounds, *i. e.* *meso*-tetraphenylporphyrin (**2H-TPP**) and Zn(II) *meso*-tetraphenylporphyrin (**Zn-TPP**), in CH_2Cl_2 . The main electrochemical parameters are collected in Table 1 and the relevant cyclic and square wave voltammograms are shown in Figures S10-12. Redox potentials of **2H-TPP** and **Zn-TPP** are in agreement with literature reports.⁵¹ All free-base and Zn derivatives display two reversible or quasi-reversible mono-electronic oxidation waves, as generally observed in porphyrin systems, corresponding to the abstraction of an electron from the π -electron core of the porphyrin. As expected, the coordination of the Zn^{2+} cation to the free-base porphyrin leads to a cathodic shift of the oxidation potentials of both waves since it increases the electron density of the porphyrin macrocycle. Notably, this shift for the first oxidation wave is increased from ca. 0.17 V for the TPP derivatives to ca. 0.24 V for the TPyP complexes. Since the reduction of **Zn-Ref** is negatively shifted by 0.17 V compared to **ZnTPP**, this pronounced shift prevented the observation of the second reduction wave in **Zn-Ref**, which falls outside the active electrochemical window. The first oxidation potentials of **Zn-Ref** and **Zn-TPyP** are close to that of the prototypical **Zn-TPP**. In fact, whereas the first oxidation potential of **Zn-Ref** is 60 mV less positive, **Zn-TPyP** is 20 mV more positive than **Zn-TPP**. Thus, the redox properties of the Zn porphyrins presented in this study could hardly account for the observed processes upon addition of an excess of silver.

Table 1. Electrochemical data.^a

	E_{red}^1 (ΔE_{pp}), V	E_{red}^2 (ΔE_{pp}), V	E_{ox}^1 (ΔE_{pp}), V	E_{ox}^2 (ΔE_{pp}), V
2H-TPP	-2.01 (0.07)	-1.70 (0.07)	+0.52 (0.07)	+0.85 (0.07)
2H-TPyP ^b	-	n.d. ^c	+0.61 (0.07)	+1.02 (0.08)
2H-Ref	-2.09 (0.12)	-1.66 (0.12)	+0.76 (0.08)	+1.14 (0.12)
Zn-TPP	-2.23 (0.12)	-2.02 (0.08)	+0.35 (0.07)	+0.67 (0.07)
Zn-TPyP	-	n.d. ^c	+0.37 (0.07)	+0.79 (0.08)
Zn-Ref	-	-2.19 (0.08)	+0.29 (0.08)	+0.61 (0.08)

^a Potential reported vs Fc^{+/0}. ^b Data from Square Wave Voltammetry. ^c Due to the low concentration (< 10⁻⁴ M) of analyte it was not possible to safely assign the potential of the reduction wave.

Rather, the crowding effects of the methyl groups could be involved in the unusual stabilization of the Zn(II) porphyrin radical cation. A variation of the redox properties of the Ag(I) ions in the used experimental conditions (formation of aggregates and more positive reduction potential) could also explain the generation of the ZnP^{•+}. In the case of the free-base porphyrins **2H-TPyP** or **2H-Ref**, the steric constraints provided by the *meso* 2,6-dimethylphenyl groups could modify the conformation flexibility of the Ag(I)₂-porphyrin complexes as compared to the related complexes with *meso*-tetraphenyl type porphyrins and prevent the formation of Ag(II)-porphyrin.

Conclusions

The formation of the coordination cages [Ag₄(**2H-TPyP**)₂]⁴⁺ and [Ag₄(**Zn-TPyP**)₂]⁴⁺ needs a strict control on the amount of added Ag⁺ ion. The cages form with high association constants upon the addition of two equivalents of Ag(I) salt but they re-open when the amount of added ions reaches four equivalents. An excess of Ag⁺ ions triggers different side reactions depending whether we deal with the free-base or Zn-metalated porphyrin. **2H-TPyP** undergoes a metalation reaction leading to a Ag(I)₂-porphyrin complex whereas **Zn-TPyP** undergoes an oxidation process with the formation of a stable radical cation. These processes, identified by means of detailed spectroscopic analysis, occur also in the models **2H-Ref** and **Zn-Ref**, devoid of polyether substituted pyridyl residues and containing methoxy and triflate groups. The formation of species which are generally instable and hardly characterizable allowed to gain interesting information on their luminescence features. The occurrence of these unusual side processes, which has to be ascribed to the *meso* ortho-dimethylphenyl porphyrin substituents, opens new perspectives in the design of Ag(I)/porphyrin based coordination systems.

Experimental

Materials and reagents

All chemicals were of the best commercially available grade and used without further purification. Spectroscopic grade DCM and methanol were used for the synthesis. Chloroform and dichloromethane were freshly distilled over CaCl₂ and CaH₂, respectively. Thin layer chromatography was carried out using pre-coated polymeric sheets of silica gel (Macherey-Nagel, POLYGRAM, SIL G/UV₂₅₄).

General methods

Mass spectra were obtained by using a Bruker MicroTOF spectrometer (ES-MS).

Nuclear Magnetic Resonance (NMR) spectra for ¹H and ¹³C were acquired on Bruker AVANCE 300 and 400 spectrometers. The spectra were referenced to residual proton-solvent references (¹H: CDCl₃ at 7.24 ppm and CD₂Cl₂ at 5.32 ppm). In the assignments, the chemical shift (in ppm) is given first, followed, in brackets, by the assignment, the multiplicity of the signal (s: singlet, d: doublet), the value of the coupling constants in Hertz if applicable, and finally the number of protons implied.

Synthesis

2H-Ref has been prepared as already reported.^{35,52}

Zn-Ref preparation started with the synthesis of the free-base porphyrin, obtained according to Lindsey's procedure⁵³, as described below. 2,6-Dimethyl-4-methoxybenzaldehyde was obtained from 4-bromo-3,5-dimethylmethoxyphenyl synthesized using the procedure published by Scanlan.⁵⁴ 4-bromo-3,5-dimethylmethoxyphenyl was then converted into 2,6-dimethyl-4-methoxybenzaldehyde by the method described by Coppola⁵⁵ in 98% yield.

meso-tetrakis(2,6-dimethyl-4-methoxyphenyl)porphyrin. 100 mg (0.61 mmol) of 2,6-dimethyl-4-methoxybenzaldehyde were dissolved in 61 mL of distilled chloroform. 42.5 μ L (0.61 mmol, 1 eq) of distilled pyrrole were added, the mixture was submitted to three vacuum-argon cycles, then 244 μ L (0.61 mmol, 1 eq) of a 2.5 M solution of BF₃·OEt₂ were introduced. After 1h30 stirring at room temperature, 104 mg of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0.46 mmol, 0.75 eq) were added and mixed for about 1h. After cooling down to room temperature 169 μ L (1.22 mmol) of triethylamine were added to neutralize BF₃·OEt₂. The solvents were then evaporated to dryness, and the crude material was purified by column chromatography on silica gel (pentane/CH₂Cl₂, 50/50 to 20/80), washed with methanol and pentane, and dried under vacuum. 30 mg of a purple solid was obtained (23% yield). ¹H NMR (CDCl₃, 400 MHz): δ = -2.50 (s, 2H, N-H), 1.87 (s, 24H, Ar-CH₃), 4.06 (s, 12H, Ar-OCH₃), 7.01 (s, 8H, H_{ar}), 8.65 (s, 8H, H_{pyr}). ES-MS: m/z = found 847.41 [M+H⁺], calculated 847.42 for C₅₆H₅₅N₄O₄. ¹³C NMR (CDCl₃, 100 MHz): δ = 158.5, 155.2, 140.7, 137.4, 133.3, 126.7, 116.6, 111.9, 55.4, 22.2. UV-visible (CH₂Cl₂): λ_{max} nm: 419, 514, 547.5, 590.5, 646.5.

Zn-Ref. In a round bottom flask containing *meso*-tetrakis(2,6-dimethyl-4-methoxyphenyl)porphyrin (31 mg, 0.037 mmol, 1

eq) in distilled dichloromethane (6 mL), a solution of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (35 mg, 0.16 mmol, 4.3 eq) in methanol (1 mL) was added. The mixture was protected from light and refluxed for 4 days. After evaporation of the solvents, the reaction mixture was dissolved in dichloromethane and washed with water. The organic layer was dried over sodium sulfate, filtered and evaporated to dryness. The crude compound was purified by column chromatography on silica gel using pentane and dichloromethane (20/80) as the mobile phase. **Zn-Ref** was isolated in 65 % yield as a pink solid (22 mg). ^1H NMR (400 MHz, CD_2Cl_2): δ = 1.85 (s, 24H, Ar- CH_3), 4.04 (s, 12H, Ar- OCH_3), 7.02 (s, 8H, H_{ar}), 8.70 (s, 8H, H_{pyr}). ES-MS: m/z = found 908.33 [M^+], calculated 908.33 for $\text{C}_{56}\text{H}_{52}\text{N}_4\text{O}_4\text{Zn}$. ^{13}C NMR (126 MHz, CD_2Cl_2): δ = 159.9, 150.7, 141.2, 135.1, 131.4, 118.7, 112.7, 55.9, 22.3. UV-visible (CH_2Cl_2): λ_{max} nm: 421, 512, 550, 586.

Absorption and emission spectroscopy

Spectroscopic grade CH_2Cl_2 and DMF used were from C. Erba and Sigma-Aldrich, respectively. Treatment of CH_2Cl_2 with anhydrous potassium carbonate was performed immediately before use to remove traces of HCl, which can determine photostability of the porphyrins. $[\text{Ag}(\text{SbF}_6)]$ was from Alfa Aesar. Solutions of $[\text{Ag}(\text{SbF}_6)]$ were prepared by weighting the salt after drying it overnight under vacuum in the presence of P_2O_5 . This procedure was made necessary by its high hygroscopicity. $[\text{Ag}(\text{SbF}_6)]$ solutions were used fresh and kept in the dark during the measurements, a precaution due to the high photosensitivity of $\text{Ag}(\text{I})$ salts.

Absorption spectra were recorded with a Perkin–Elmer Lambda 650 UV-VIS and a Perkin–Elmer Lambda 950 UV-VIS-NIR spectrophotometers. Emission spectra, uncorrected if not otherwise specified, were collected with a Edinburgh FLS920 fluorimeter, equipped with Peltier-cooled Hamamatsu R928 PMT (200–850 nm). Corrected excitation spectra were recorded with the same fluorimeter. Emission quantum yields were evaluated from the area of the luminescence spectra, corrected for the photomultiplier response, with reference to tetraphenylporphyrin in aerated toluene ($\phi_{\text{f}} = 0.11$).⁵⁶

Titration experiments were performed by incremental addition of micro aliquots of stock solutions of $[\text{Ag}(\text{SbF}_6)]$ (10^{-2} – 10^{-4} M) to a ca. 1.0×10^{-5} M solution of the porphyrin. The final volume added was kept below 10% of the total volume, to avoid dilution of the porphyrin. Absorption titration experiments made use of both 1 and 0.2 cm optical path cells whereas luminescence titrations were carried out on 1 cm optical path cells. Excitation was performed at a wavelength where the absorbance remained almost the same for all the families of absorption curves detected. In case of slight variation of absorbance the emission spectra have been corrected accordingly. Titration experiments were performed avoiding light exposure of the solutions.

Fluorescence lifetimes in the nanosecond range were detected by an IBH Time Correlated Single Photon Counting apparatus with Nano-LED excitation at 465 nm. Analysis of the decay profiles against time was performed using the Decay Analysis Software DAS6 provided by the manufacturer.

Estimated errors are 10% on lifetimes, 20% on quantum yields, 20% on molar absorption coefficients and 3 nm on emission and absorption peaks.

Electrochemistry

Cyclic and square wave voltammograms were recorded with a Metrohm Autolab PG-STAT 302 electrochemical workstation operated with the NOVA 2.0 software package. All measurements were carried out in dry CH_2Cl_2 (VWR, Uvasol®) solutions containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate (Sigma-Aldrich, electrochemical grade) and ca. 2×10^{-4} M analyte under a dry nitrogen atmosphere, at scan rate $v = 100 \text{ mV s}^{-1}$. A single-compartment three electrode cell was equipped with platinum wire counter and pseudo-reference electrodes and a glassy carbon working electrode (BioLogic). All redox potentials are reported with respect to the ferrocene/ferrocenium (Fc/Fc^+) redox couple, added at the end of each experiment, used as internal reference system.

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‡ The emission spectra have been corrected for the slight change in absorbance of the solutions at this wavelength.

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