Copper(I) complexes of 1,10-phenanthroline–oligophenylenevinylene conjugates

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Copper(I) complexes obtained from 2,9-diphenyl-1,10-phenanthroline derivatives substituted with an oligophenylenevinylene (OPV) unit have been prepared. Very strong intramolecular quenching of the lowest OPV excited state by the copper(I) complex has been evidenced in these multicomponent systems. The mechanism of the photoinduced process depends on the length of the conjugated OPV backbone. Upon irradiation of the OPV unit, quantitative sensitization of the Cu(I) complex has been evidenced for the system substituted with trimeric OPV units, but not for those with tetrameric OPV units. Therefore, energy transfer is the sole quenching mechanism for the former complex, whereas electron transfer might play a role in the latter case. This different behaviour is ascribed to the slightly increased electron-accepting character of the OPV tetrameric unit when compared to the corresponding trimer. As far as excited state deactivation in the copper(I) complex is concerned, the hybrid compounds exhibit the characteristic luminescence band attributable to the deactivation of low-lying metal-to-ligand charge transfer (MLCT) excited state(s). As shown by the comparison with a model copper(I) complex, the OPV units have no influence on the MLCT excited state(s) deactivation at room temperature in fluid solutions. In contrast, they are capable of acting as "hooks" when the measurements are performed at low temperature in a rigid matrix, thus reducing the excited state distortion of the copper(I) complex. As a result, at 77 K the MLCT emission spectral shapes and band maxima of the hybrid compounds are no longer identical to those of the corresponding model complex.

Introduction

π-Conjugated oligomers have been extensively investigated over the past years owing to their ability to model the electronic properties of their parent polymers.[1–6] If one important challenge of this research is to comprehensively investigate many physical properties relevant to materials science (charge transport, nonlinear optical effects, *etc.*),[1–7] the characteristic features of these compounds make them also versatile photo- and/or electro-active components for the preparation of photochemical molecular devices.[8–19] In fact, π-conjugated oligomers possess a broad range of attractive optical properties as well as the ability to accept or donate charges. In addition, their physical properties can be easily modulated by changing the length of the conjugated backbone or the nature of the substituents.[8–20] As part of this research, we have developed efficient synthetic procedures for the synthesis of oligophenylenevinylene (OPV) building blocks and shown that they can be useful for the preparation of molecular devices that perform light-induced functions such as electron or energy transfer.[14–21] For example, photophysical studies of a two-component system combining an OPV trimer unit with a 1,10-phenanthroline moiety, which can be protonated, have revealed that this hybrid compound can act as a proton-triggered molecular switch. Actually, the direction of the intramolecular photoinduced energy transfer can be tuned by proton input, thus allowing on/off switching of the luminescence of the OPV moiety.[16] In this paper, we now report the preparation of the copper(I) complex $Cu^+(Phen\text{-}3PV)_2$ obtained from this 1,10-phenanthroline–OPV conjugate (Fig. 1). In addition, the higher homologue $Cu^+(Phen\text{-}4PV)_2$ substituted with OPV tetrameric moieties is also described (Fig. 1). The photophysical properties of $Cu^+(Phen\text{-}3PV)_2$ and $Cu^+(Phen\text{-}4PV)_2$ have been investigated and compared to those of the corresponding model compounds 3PV, 4PV, $Cu^+(\mathbf{3})_2$ and $Cu^+(\mathbf{7})_2$ (Fig. 2). Interestingly, whereas quantitative photoinduced energy transfer from the lowest OPV excited state to the copper(I) bis(1,10-phenanthroline) $[Cu^+(phen)_2]$ complex has been evidenced for $Cu^+(Phen\text{-}3PV)_2$, both energy and electron transfer quenching mechanisms are involved for $Cu^+(Phen\text{-}4PV)_2$. Furthermore, the photophysical properties of the various $Cu^+(phen)_2$ complexes have been studied in detail. Differences observed in the metal-to-ligand-charge-transfer (MLCT) emission properties, especially at 77 K, are ascribed to structural factors affecting the excited state coordination geometry.[22–29]

Results and discussion

Synthesis

The synthetic approach to prepare the OPV-substituted phenanthroline derivatives Phen-3PV and Phen-4PV is based on

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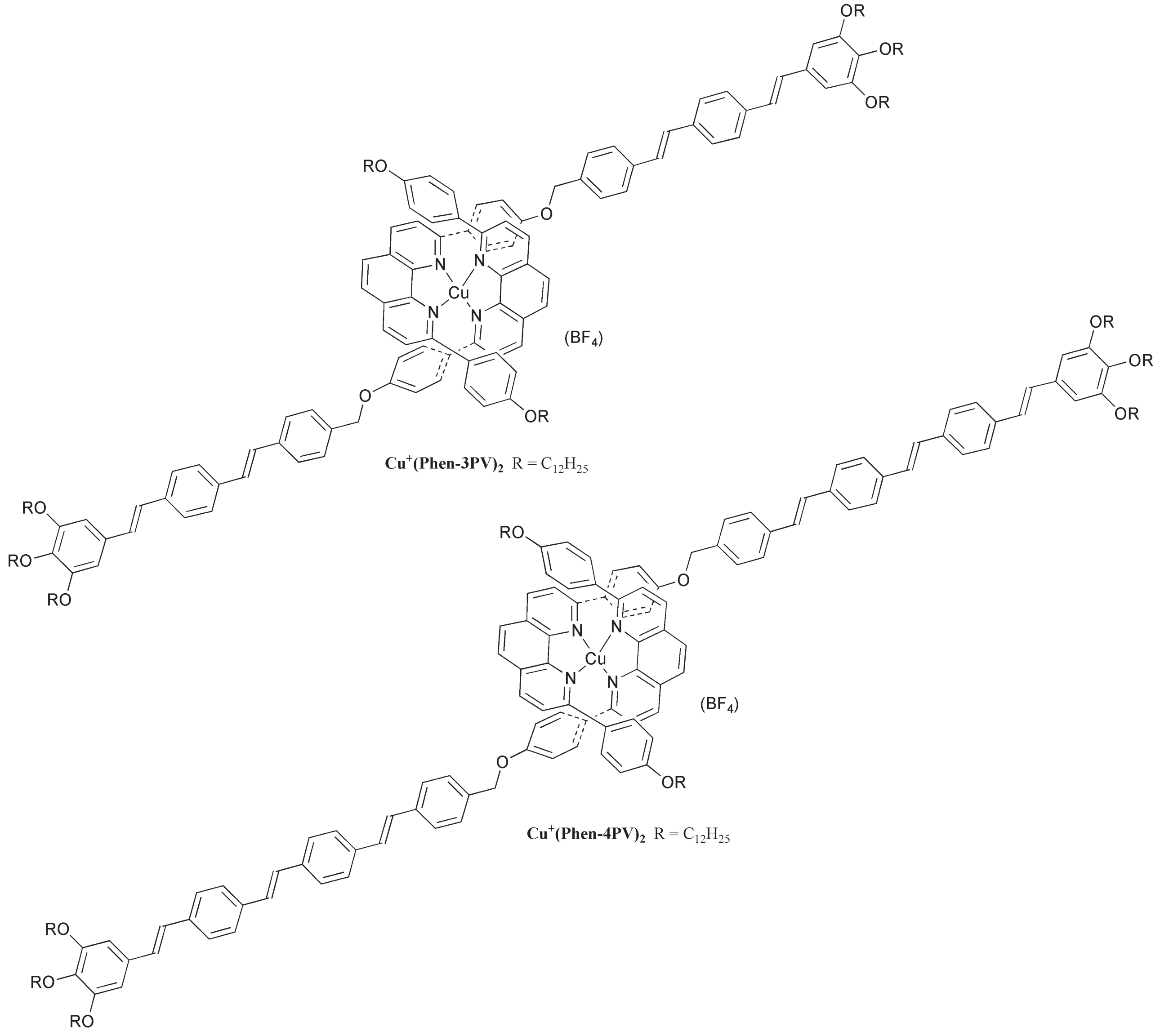


$Cu^+(Phen\text{-}3PV)_2$ $R = C_{12}H_{25}$

$Cu^+(Phen\text{-}4PV)_2$ $R = C_{12}H_{25}$

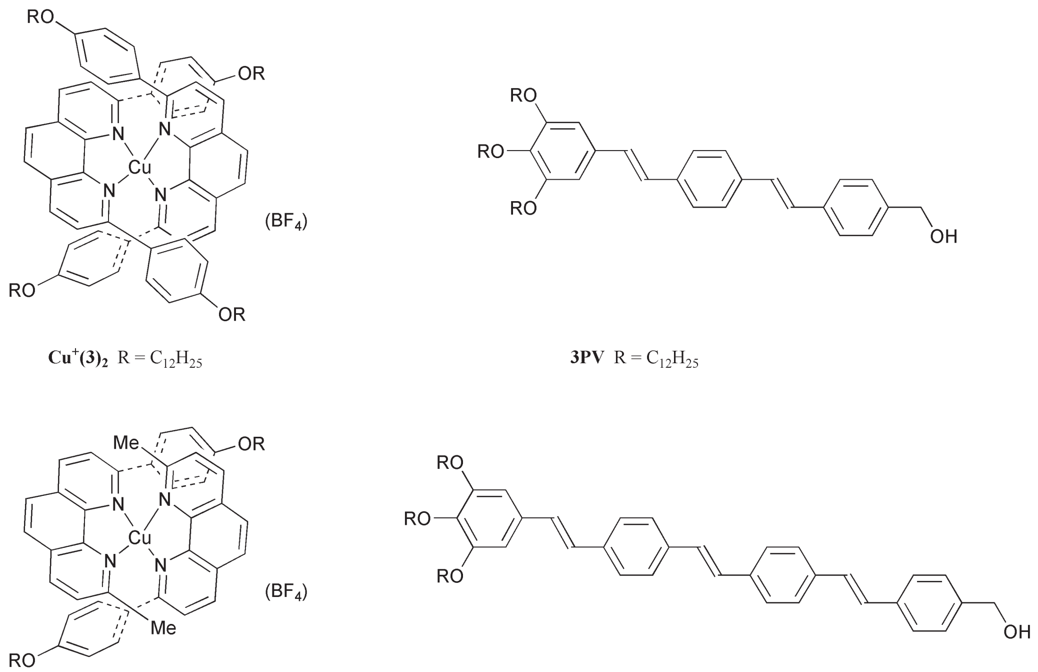
Fig. 1 $Cu^+(phen)_2$ complexes with appended OPV units.

the functionalization of precursor **6** with the OPV building blocks 3PV and 4PV under Mitsunobu conditions. The preparation of key intermediate **6** is depicted in Scheme 1. Reaction of 1,10-phenanthroline with *p*-lithiododecyloxyphenyl under the conditions developed by Sauvage and co-workers[30] gave **2** in 85% yield together with a small amount of the disubstituted derivative **3** (2%). Treatment of **2** with *p*-lithio[(*tert*-butyldimethylsilyl)oxy]phenyl[31] at 0 °C followed by hydrolysis and re-aromatization with MnO_2 yielded **5** in 33%. Subsequent treatment with tetra-*n*-butylammonium fluoride (TBAF) in THF at 0 °C then gave compound **6** in quantitative yield.

Ligands Phen-3PV and Phen-4PV were then obtained by treatment of **6** with 3PV and 4PV, respectively, in the presence of diethyl azodicarboxylate (DEAD) and triphenylphosphine in refluxing THF under Mitsunobu conditions (Scheme 2).[32] It is worth noting that the choice of the Mitsunobu reaction for the preparation of the Phen–OPV derivatives was the key to their synthesis. The first attempted synthetic route for the preparation of these compounds was based on the alkylation of phenol **6** with the benzylic bromides or chlorides derived from 3PV and 4PV. However, these benzylic halides were found to be unstable and difficult to handle.[33] Therefore, the Mitsunobu reaction appeared as an appropriate alternative since it allowed the *in situ* activation of the benzylic alcohols 3PV and 4PV, thus preventing the use of unstable intermediates.

The copper(I) complexes $Cu^+(\mathbf{3})_2$, $Cu^+(Phen\text{-}3PV)_2$ and $Cu^+(Phen\text{-}4PV)_2$ were obtained in good yields by treatment of the corresponding ligands with $Cu(CH_3CN)_4BF_4$ in CH_2Cl_2 at room temperature. The coordination of the ligands to the copper(I) cation could be easily observed by the appearance of the metal-to-ligand charge transfer (MLCT) band characteristic of bis(2,9-dipheny-1,10-phenanthroline) copper(I) derivatives (see below). Furthermore, their ^1H-NMR spectra also provided good evidence for their formation. The signals of the protons belonging to the phenyl rings attached to the phenanthroline core observed at *ca.* 8.4 and 7.1 ppm in the ligands are shifted to *ca.* 7.4 and 6.1 ppm in the corresponding complexes. This particular behaviour is specific of such copper(I) complexes and is the result of the ring current effect of one phenanthroline subunit on the 2,9-substituents of the second one in the complex.[34]

In addition, the copper(I) complex $Cu^+(\mathbf{7})_2$ used as a reference compound for the photophysical studies was prepared by treatment of ligand **7** with $Cu(CH_3CN)_4BF_4$. The disubstituted phenanthroline derivative **7** was obtained by reaction of **2** with MeLi followed by hydrolysis and re-aromatization with MnO_2 (Scheme 3).



Cu$^+$(3)$_2$ R = $C_{12}H_{25}$

3PV R = $C_{12}H_{25}$

Cu$^+$(7)$_2$ R = $C_{12}H_{25}$

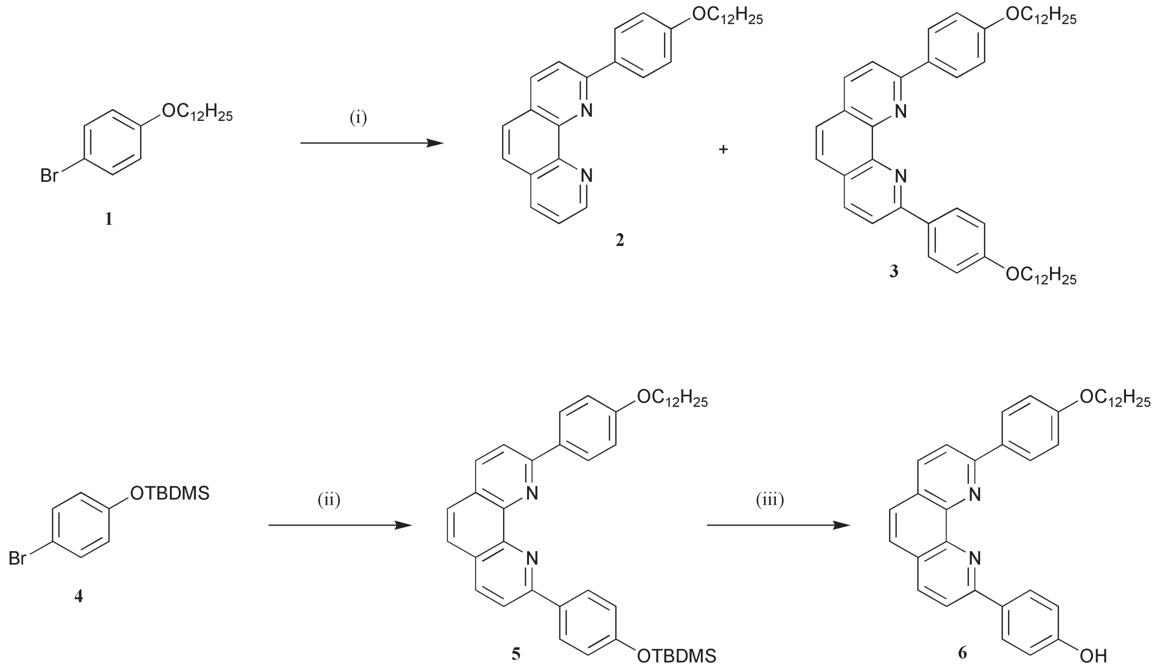
4PV R = $C_{12}H_{25}$

Fig. 2 Reference compounds.

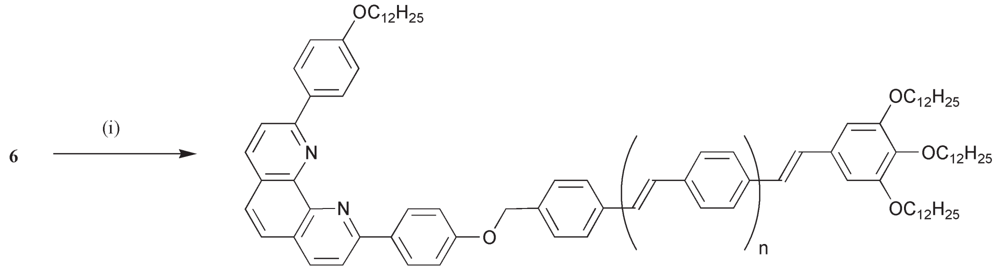
Electrochemistry

The electrochemical properties of 3PV, 4PV, Cu$^+$(**3**)$_2$, Cu$^+$(**7**)$_2$, Cu$^+$(Phen-3PV)$_2$ and Cu$^+$(Phen-4PV)$_2$ were investigated by cyclic voltammetry (CV) in $CH_2Cl_2 + 0.1$ M nBu$_4$NPF$_6$ solutions (Table 1).

In the cathodic scan, all the Cu$^+$(phen)$_2$ complexes show the characteristic reduction centred on the 1,10-phenanthroline ligand.[35] In the anodic region, the copper(I) complex Cu$^+$(Phen-3PV)$_2$ shows a reversible one-electron process followed by a bielectronic peak. As shown by the comparison with model compounds 3PV and Cu$^+$(**3**)$_2$, the first wave is assigned to the oxidation of the copper(I) centre while the second one corresponds to the simultaneous oxidation of the two OPV moieties. Interestingly, a positive shift (110 mV) is observed for the OPV-based oxidation of Cu$^+$(Phen-3PV)$_2$ with respect to the corresponding OPV model compound 3PV. Rather than being a consequence of strong electronic interactions between the OPV moieties and the metal centre in Cu$^+$(Phen-3PV)$_2$, the more difficult oxidation observed for the two OPV subunits is attributed to electrostatic effects resulting from the proximity of the oxidized copper complex. For Cu$^+$(Phen-4PV)$_2$, only the metal-centered oxidation was clearly observed. Due to electrode inhibition phenomena



Scheme 1 Reagents and conditions: (i) t-BuLi, THF, −78 to 0 °C, then 1,10-phenanthroline, THF, 0 °C, then H_2O, then MnO_2 (**2**: 85%, **3**: 2%); (ii) n-BuLi, THF, −78 to 0 °C, then **2**, THF, 0 °C, then H_2O, then MnO_2 (33%); (iii) TBAF, THF, 0 °C (99%).



Phen-3PV (n = 1)

Phen-4PV (n = 2)

Scheme 2 Reagents and conditions: (i) 3PV or 4PV, DEAD, PPh_3, THF, Δ (Phen-3PV: 71% from 3PV; Phen-4PV: 65% from 4PV).

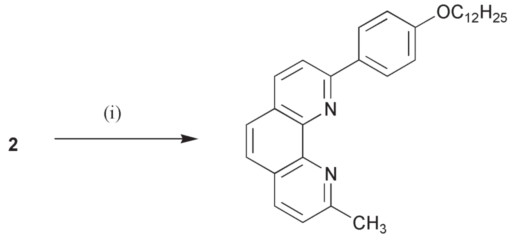
resulting from irreversible deposition onto the electrode surface, the oxidation wave corresponding to the OPV units was ill-defined and the corresponding redox potential could not be determined. Finally, the oxidation potential of 4PV is slightly shifted to a more negative value when compared to 3PV. As previously observed for related OPV derivatives, both the electron-accepting and the electron-donating ability of OPV molecules is slightly increased by increasing the conjugation length.[17,20] Even if the difference is small, it may affect the trend of photoinduced processes as far as electron transfer is concerned (see below).

Photophysical properties

The electronic absorption spectra of $Cu^+(\mathbf{3})_2$, Cu^+(Phen-3PV)$_2$, and Cu^+(Phen-4PV)$_2$ in CH_2Cl_2 solution are displayed in Fig. 3.

The ligand-centred UV spectral features and the broad and almost featureless MLCT bands above 400 nm are typical for 2,9-diphenyl-1,10-phenanthroline type copper(I) complexes.[36–38] Cu^+(Phen-3PV)$_2$ and Cu^+(Phen-4PV)$_2$ exhibit characteristic strong absorption bands centred at, respectively, 360 and 390 nm, attributable to the appended OPV residues (Fig. 4).[16]

In the UV region the absorption spectra of Cu^+(Phen-3PV)$_2$ and Cu^+(Phen-4PV)$_2$ satisfactorily match, within a 10% experimental error, with the sum of the spectra of $Cu^+(\mathbf{3})_2$ and of two units of, respectively, 3PV and 4PV. An excellent overlap of the MLCT bands in the 400–700 nm region is found for $Cu^+(\mathbf{3})_2$ and Cu^+(Phen-3PV)$_2$ (Fig. 3), whereas the apparent MLCT band broadening for Cu^+(Phen-4PV)$_2$, relative to its model compounds, is substantially due to the contribution of the absorption tail of the 4PV fragments towards the visible spectral side (Fig. 4). These results show that: (i) no strong ground state electronic interactions between the Cu^+(phen)$_2$ core and the appended OPVs take place and (ii) the OPV fragments are too peripheral to affect the ground state geometry of the complexes and, consequently, the MLCT electronic absorption band profiles. The latter result is interesting since it is known that, at closer distances from the coordination centre, very small changes of the phenanthroline substituents bring about marked variations of the absorption spectral shapes.[35]



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Scheme 3 Reagents and conditions: (i) MeLi, Et_2O, 0 °C, then H_2O, then MnO_2 (74%).

The MLCT luminescence data of $Cu^+(\mathbf{3})_2$, $Cu^+(\mathbf{7})_2$, Cu^+(Phen-3PV)$_2$, and Cu^+(Phen-4PV)$_2$ in CH_2Cl_2 at 298 and 77 K, along with some related quantities, are collected in Table 2; data for $Cu^+(\mathbf{3})_2$ and $Cu^+(\mathbf{7})_2$ are listed for reference purposes.

All the complexes show the typical emission band around 700 nm, attributable to the deactivation of MLCT excited states (Figs. 5 and 6).[23,39] At 298 K, the photophysical parameters of $Cu^+(\mathbf{3})_2$, Cu^+(Phen-3PV)$_2$ and Cu^+(Phen-4PV)$_2$ reported in Table 2 are identical within the experimental uncertainties. This suggests that OPV fragments do not affect the excited state properties of the Cu^+(phen)$_2$ core, in analogy with the ground state behaviour (see above). Cu(I) bis(phenanthroline) complexes are known to undergo extensive conformational rearrangements in the MLCT excited state,[22] whose extent is strongly dependent on the chemical nature and bulkiness of the phenanthroline substituents.[23,24] The present results show that the OPV units are too far from the coordination centre to be able to influence the excited state distortion. In other words the "effective" coordination centre of Cu^+(Phen-3PV)$_2$ and Cu^+(Phen-4PV)$_2$ is the same as for $Cu^+(\mathbf{3})_2$, that is Cu^+(dap)$_2$ [dap = 2,9-di(*p*-alkyloxyphenyl)-1,10-phenanthroline].

The influence of the substituents directly attached to the phenanthroline unit is evidenced by the photophysical properties of $Cu^+(\mathbf{7})_2$. In this complex, the ligand is asymmetric as in Cu^+(Phen-3PV)$_2$ and Cu^+(Phen-4PV)$_2$; one phenanthroline substituent is the same as in $Cu^+(\mathbf{3})_2$, while the other one is a methyl group (Fig. 2). $Cu^+(\mathbf{7})_2$ is a weaker luminophore than the other complexes here investigated, thus showing the strong effect due to the presence of the methyl group. Such a small substituent favours excited state distortions and offers scarce protection from excited state deactivation by external

Table 1 Electrochemical properties determined by CV on a glassy carbon working electrode in CH_2Cl_2 + 0.1 M nBu$_4$NPF$_6$ solutions at room temperature

	Reduction	Oxidation	
	E_1	E_1	E_2
3PV		+0.57[a]	
4PV	−2.35[b]	+0.54[a]	
Cu(**3**)$_2$	−2.26[b c]	+0.27[a]	
Cu(**7**)$_2$	−2.07[b c]	+0.33[a]	
Cu(Phen-3PV)$_2$	−2.25[b]	+0.25[a]	+0.68[d]
Cu(Phen-4PV)$_2$	−2.21[b]	+0.28[a]	—[e]

[a] Values for $(E_{pa} + E_{pc})/2$ in V *vs.* Fc^+/Fc at a scan rate of 0.1 V s^{-1}. [b] Irreversible process, E_{pa} value reported. [c] Reversible for $v > 1$ V s^{-1}. [d] Dielectronic process. [e] Not resolved.

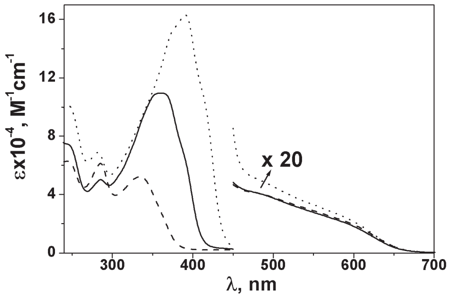

Fig. 3 Absorption spectra $Cu^+(\mathbf{3})_2$ (dashed line), Cu^+(Phen-3PV)$_2$ (solid line) and Cu^+(Phen-4PV)$_2$ (dotted line) in CH_2Cl_2 solution at 298 K. Over the 450-700 nm region a multiplying factor of 20 is applied.

molecules (solvent, counterions, dioxygen), which is the most common excited state non-radiative deactivation path for Cu^+(phen)$_2$ complexes.[40] The latter effect is also reflected in the high Stern–Volmer quenching rate constant by dioxygen of $Cu^+(\mathbf{7})_2$, when compared to those of the other complexes presented here (Table 2).

On passing from fluid solution (Fig. 5) to a 77 K rigid matrix (Fig. 6), the MLCT emission spectral shapes and maxima of $Cu^+(\mathbf{3})_2$, Cu^+(Phen-3PV)$_2$ and Cu^+(Phen-4PV)$_2$ are no longer identical. At 77 K the reference compound $Cu^+(\mathbf{3})_2$ exhibits a marked spectral red-shift and intensity decrease relative to the room temperature spectrum; this is typical for Cu(I) diphenylphenanthroline type complexes and is rationalized on the basis of the so-called two-level model.[41,42] According to this model, emission at 77 K stems from a low-lying poorly emitting MLCT triplet (^{3}MLCT), whose population is depleted at higher temperatures as a consequence of a thermal equilibrium with an upper lying singlet (^{1}MLCT) exhibiting stronger luminescence. We have recently shown by temperature dependent luminescence studies that the interplay between these two levels is determined by electronic and structural factors with the latter, related to specific distortions from the ideal tetrahedral geometry in the ground and excited state related to the nature of the substituents of the chelating ligand, playing a major role.[43] In fact, the substituents on the phenanthroline ligands strongly affect the coordination geometry at 77 K, in turn governing the luminescence performances. The results reported in the present paper confirm this conclusion. The geometry of the excited state is very similar, if not identical, for $Cu^+(\mathbf{3})_2$, Cu^+(Phen-3PV)$_2$ and Cu^+(Phen-4PV)$_2$ at room temperature, as deduced by the luminescence results. The different behaviour observed at 77 K is hardly ascribable to electronic factors induced by the substituents, which are likely to be identical as suggested by the room temperature photophysical properties (see above). The less marked red-shift and intensity decrease of the emission bands of Cu^+(Phen-3PV)$_2$ and Cu^+(Phen-4PV)$_2$, relative to the model compound $Cu^+(\mathbf{3})_2$, indicate a reduced excited state distortion in the rigid matrix brought about by the OPV appended fragments. It is conceivable that in such compounds the OPV groups protrude into the rigid matrix, thus acting as "hooks" capable of reducing structural distortion.

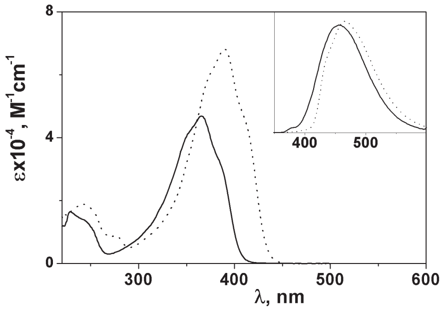

Fig. 4 Absorption and (inset) normalized fluorescence spectra of 3PV (solid line) and 4PV (dotted line) in CH_2Cl_2. Luminescence profiles are recorded at 298 K upon excitation at 320 nm with absorbance of 0.10 for both samples.

At 298 K excitation of Cu^+(Phen-3PV)$_2$ and Cu^+(Phen-4PV)$_2$ in the OPV absorption maxima (360 and 390 nm, respectively) reveals a 60-fold quenching of the strong OPV fluorescence[16,17,44,45] in both cases, relative to the reference compounds 3PV ($\Phi_{\text{fluo}} = 0.77$)[16] and 4PV ($\Phi_{\text{fluo}} = 0.66$). Photoinduced energy transfer from the lowest OPV singlet excited state (^{1}OPV*) to the MLCT excited state centred on the Cu(I) complexed moiety may be responsible for the observed quenching. From the 77 K emission spectra (Figs. 4 and 6, Table 2), which allow a reasonable estimation of the energy of the emitting excited states of each moiety, one can derive a thermodynamic driving force of 1.13 (Cu^+(Phen-3PV)$_2$) and 0.95 (Cu^+(Phen-4PV)$_2$) eV for such processes.[36]

In order to confirm the occurrence of energy transfer, sensitization of the Cu^+(phen)$_2$ MLCT luminescence by the appended OPVs should be detected. In practice, this is difficult to observe because the residual luminescence of the latter is strong enough to overlap the weak emission of the former for both Cu^+(Phen-3PV)$_2$ and Cu^+(Phen-4PV)$_2$. Therefore, precise quantitative estimates of sensitization cannot be made. Having in mind the above limitations, we subtracted the OPV background signal and could estimate a quantitative sensitization of the Cu(I) complexed moiety in Cu^+(Phen-3PV)$_2$, but only a 70% sensitization in the case of Cu^+(Phen-4PV)$_2$. This suggests that in Cu^+(Phen-3PV)$_2$ energy transfer is the only intramolecular process, whereas in Cu^+(Phen-4PV)$_2$ electron transfer quenching might also play a role. The energy required for oxidation of the metal centre (Table 1) and reduction of the OPV moieties[46] can be estimated to be about 2.7 eV[47] and is comparable to the excited state energy of the 3PV and 4PV singlet states (2.6–2.8 eV, from 77 K fluorescence spectra). Since 4PV is a better electron acceptor than the shorter 3PV[17,20] this could result in some contribution from electron transfer quenching.

Conclusions

Multicomponent systems combining OPV units with a Cu^+(phen)$_2$ moiety have been prepared. Very strong intramolecular quenching of the lowest OPV excited state by the copper(I) complex has been evidenced in these systems. In Cu^+(Phen-3PV)$_2$ quantitative sensitization of the Cu(I) complex has been evidenced, suggesting that energy transfer is the only quenching mechanism. In the case of Cu^+(Phen-4PV)$_{2,}$, electron transfer is also likely to be involved. This different behaviour is ascribed to the slightly increased electron-accepting character of the OPV tetrameric unit when compared to the corresponding trimer. As far as the Cu^+(phen)$_2$ excited state deactivation is concerned, both Cu^+(Phen-3PV)$_2$ and Cu^+(Phen-4PV)$_2$ exhibit the characteristic luminescence band attributable to the deactivation of low-lying MLCT excited state(s). The comparison with the corresponding model compound $Cu^+(\mathbf{3})_2$ is of particular interest. Whereas the OPV units have no influence on the room temperature emission properties in fluid solution, remarkable differences are found for the 77 K luminescence spectra. The stronger emission intensity and blue-shift[43] observed for the hybrid systems Cu^+(Phen-3PV)$_2$ and Cu^+(Phen-4PV)$_2$ relative to the reference compound $Cu^+(\mathbf{3})_2$ are attributed to structural factors. The OPV units can act as "hooks" protruding into the rigid matrix when the measurements are performed at low temperature, thus reducing the excited state distortion of Cu^+(Phen-3PV)$_2$ and Cu^+(Phen-4PV)$_2$. As a result, the

Table 2 Photophysical properties at 298 K (CH_2Cl_2 solution) and 77 K (1:1 CH_2Cl_2–MeOH glass)

	298 K						77 K	
	$\lambda_{max\ (em)}$/nm[a]	$10^4\ \Phi^{em}$ [b]	τ/ns[c]	$10^{-3}\ k_r/s^{-1}$ [d]	$10^{-6}\ k_{nr}/s^{-1}$ [e]	$10^6\ k_q[O_2]/s^{-1}$ [f]	$\lambda_{max\ (em)}$/nm[a]	τ/ns[c]
$Cu^+(\mathbf{3})_2$	684 (714)	8.4 (12.7)	147 (220)	5.7	6.8	2.3	742 (766)	1100
$Cu^+(\mathbf{7})_2$	684 (750)	3.2 (4.2)	7.8/73 (102)[g]	4.4	13.7	3.9	742 (770)	14/530[g]
Cu^+(Phen-3PV)$_2$	684 (714)	8.8 (12.5)	146 (221)	6.0	6.9	2.3	716 (748)	1400
Cu^+(Phen-4PV)$_2$	684 (714)	8.6 (12.2)	140 (211)	6.1	7.1	2.4	712 (746)	1100

[a] Emission maxima from uncorrected and, in parentheses, corrected spectra. [b] Emission quantum yields in air-equilibrated and, in parentheses, air-free solutions. [c] Excited state lifetimes in air-equilibrated and, in parentheses, air-free solutions. [d] Radiative decay rate constants in air-free solution. [e] Non-radiative decay rate constants in air-free solution. [f] Stern–Volmer rate constants for the quenching of the luminescent excited state by O_2, estimated from lifetimes in air-free and air-equilibrated solutions.[36] [g] Biexponential decay.

MLCT emission spectral shapes and band maxima of $Cu^+(\mathbf{3})_2$, Cu^+(Phen-3PV)$_2$ and Cu^+(Phen-4PV)$_2$ are no longer identical under these conditions.

Experimental

General methods

Reagents and solvents were purchased as reagent grade and used without further purification. THF was distilled over sodium benzophenone ketyl. Compounds **1**,[48] **4**,[31] 3PV and 4PV[18,19] were prepared as previously reported. All reactions were performed in standard glassware under an inert Ar atmosphere. Evaporation and concentration were done at water aspirator pressure and drying *in vacuo* at 10^{-2} Torr. For column chromatography silica gel 60 (230–400 mesh, 0.040–0.063 mm) was purchased from E. Merck. Thin layer chromatography (TLC) was performed on glass sheets coated with silica gel 60 F_{254} purchased from E. Merck, visualization by UV light. NMR spectra were recorded on a Bruker AC 200 (200 MHz) or a Bruker AM 400 (400 MHz) with solvent peaks as reference. FAB mass spectra (MS) were obtained on a ZA HF instrument with 4-nitrobenzyl alcohol as matrix. Elemental analyses were performed by the analytical service at the Institut Charles Sadron, Strasbourg.

Synthesis

Compounds 2 and 3. A 1.7 M solution of *t*-BuLi in hexane (21.8 mL, 37.06 mmol) was slowly added to a degassed solution of **1** (5.0 g, 18.56 mmol) in dry THF (40 mL) at −78 °C. After 30 min at −78 °C, the solution was allowed to warm up to 0 °C (over 1 h) and cooled again to −78 °C. The resulting mixture was then added, by means of a double-ended needle, to a degassed solution of 1,10-phenanthroline (2.57 g, 14.28 mmol) in dry THF (50 mL) at 0 °C. The resulting dark red solution was stirred for 3 h, then hydrolyzed with water. CH_2Cl_2 was added and the bright yellow organic layer decanted. The aqueous layer was extracted with CH_2Cl_2 (3X) and the combined organic layers were thereafter re-aromatized by addition of MnO_2 (30 g), dried ($MgSO_4$) and filtered; the filtrate was then evaporated to dryness. Column chromatography (SiO_2, CH_2Cl_2) gave **3** (200 mg, 2%) and **2** (5.39 g, 85%).

2. Pale yellow solid (mp 155 °C).^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 9.24$ (dd, $J = 4$ and 1 Hz, 1 H), 8.32 (d, $J = 8$ Hz, 2 H), 8.22 (dd, $J = 4$ and 1 Hz, 1 H), 8.15 (d, $J = 8$ Hz, 1 H), 8.05 (d, $J = 8$ Hz, 1 H), 7.75 (AB, $J = 8$ Hz, 2 H), 7.61 (dd, $J = 8$ and 1 Hz, 1 H), 7.05 (d, $J = 8$ Hz, 2 H), 4.05 (t, $J = 6.5$ Hz, 2 H), 1.83 (m, 2 H), 1.28 (m, 18 H), 0.88 (t, $J = 6$ Hz, 3 H). ^{13}C-NMR (50 MHz, $CDCl_3$): $\delta = 160.33$, 156.98, 150.15, 146.22, 146.00, 136.52, 135.91, 131.80, 129.12, 128.93, 126.98, 126.27, 125.59, 122.61, 119.80, 114.56, 67.97, 31.82, 30.40, 29.51, 29.34, 29.25, 29.18, 25.96, 22.59, 14.05. Anal. calcd for $C_{30}H_{36}N_2O$: C 81.78, H 8.24, N 6.36; found: C 81.68, H 8.22, N 6.40.

3. Pale yellow glassy product. ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 8.43$ (d, $J = 8$ Hz, 4 H), 8.27 (d, $J = 8$ Hz, 2 H), 8.09 (d, $J = 8$ Hz, 2 H), 7.75 (s, 2 H), 7.10 (d, $J = 8$ Hz, 4 H), 4.08 (t, $J = 6.5$ Hz, 4 H), 1.86 (m, 4 H), 1.28 (m, 36 H), 0.90 (t, $J = 6$ Hz, 6 H). ^{13}C-NMR (50 MHz, $CDCl_3$): $\delta = 160.40$, 156.22, 145.91, 136.59, 131.83, 128.86, 127.36, 125.44, 119.13, 114.63, 68.00, 31.84, 29.53, 29.38, 29.26, 26.00, 22.62, 14.06. Anal. calcd for $C_{48}H_{64}N_2O_2 \cdot 1/2H_2O$: C 81.19, H 9.23; N 3.95; found: C 81.37, H 9.03, N 3.76.

Compound 5. A 1.5 M solution of *n*-BuLi in hexane (3.6 mL, 5.4 mmol) was slowly added to a degassed solution of **4** (1.69 g, 5.90 mmol) in dry THF (40 mL) at −78 °C. After 30 min. at −78 °C, the solution was allowed to warm up to 0 °C (over 1 h) and cooled again to −78 °C. The resulting mixture was then added, by means of a double-ended needle, to a degassed solution of **2** (2.0 g, 4.53 mmol) in dry THF (50 mL) at 0 °C. The

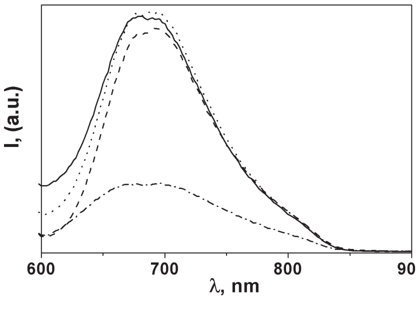

Fig. 5 Luminescence spectra of $Cu^+(\mathbf{3})_2$ (dashed line), $Cu^+(\mathbf{7})_2$ (dotted-dashed line), Cu^+(Phen-3PV)$_2$ (dotted line) and Cu^+(Phen-4PV)$_2$ (solid line) in CH_2Cl_2 solution at 298 K upon excitation at 500 nm (isoabsorbing solutions with $A = 0.12$).

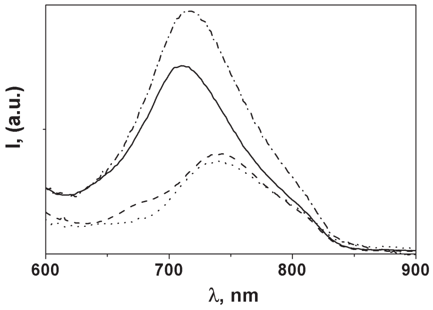

Fig. 6 Luminescence spectra of $Cu^+(\mathbf{3})_2$ (dashed line), $Cu^+(\mathbf{7})_2$ (dotted line), Cu^+(Phen-3PV)$_2$ (dotted-dashed line) and Cu^+-(Phen-3PV)$_2$ (solid line) in CH_2Cl_2–MeOH (1:1) glass at 77 K upon excitation at 500 nm. The absorbance of the solutions before cooling was identical (0.370).

resulting dark red solution was stirred for 3 h, then hydrolyzed with water. CH_2Cl_2 was added and the bright yellow organic layer decanted. The aqueous layer was extracted with CH_2Cl_2 (3X) and the combined organic layers were thereafter re-aromatized by addition of MnO_2 (30 g), dried ($MgSO_4$) and filtered; the filtrate was then evaporated to dryness. Column chromatography (SiO_2, CH_2Cl_2) gave **5** (950 mg, 33%) as a pale yellow glassy product. ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 8.43$ (d, $J = 8$ Hz, 2 H), 8.37 (d, $J = 8$ Hz, 2 H), 8.26 (d, $J = 8$ Hz, 2 H), 8.08 (d, $J = 8$ Hz, 2 H), 7.74 (s, 2 H), 7.11 (d, $J = 8$ Hz, 2 H), 7.05 (d, $J = 8$ Hz, 2 H), 4.08 (t, $J = 6.5$ Hz, 2 H), 1.80–1.70 (m, 2 H), 1.50–1.20 (m, 18 H), 1.04 (s, 9 H), 0.90 (t, $J = 6.5$ Hz, 3 H), 0.28 (s, 6 H). ^{13}C-NMR (50 MHz, $CDCl_3$): $\delta = 160.50$, 157.20, 156.41, 146.00, 136.72, 132.88, 131.89, 128.94, 127.47, 125.64, 125.54, 120.52, 119.38, 119.29, 114.69, 68.09, 31.93, 26.09, 25.73, 22.70, 18.30, 14.15, −4.32.

Compound 6. A 1 M solution of TBAF (2.20 mmol, 2.20 ml) was added to a solution of **5** (950 mg, 1.46 mmol) in THF (15 mL) at 0 °C. After 1.5 h, a saturated NH_4Cl aqueous solution was added and the THF evaporated. The aqueous layer was extracted with CH_2Cl_2 (3X). The combined organic layers were dried ($MgSO_4$), filtered and evaporated to dryness. Column chromatography (SiO_2, CH_2Cl_2–MeOH 99:1) gave **4** (777 mg, 99%) as a red solid that was used in the next step without further purification. ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 8.41$ (d, $J = 8$ Hz, 2 H), 8.33 (d, $J = 8$ Hz, 2 H), 8.27 (d, $J = 8$ Hz, 2 H), 8.08 (d, $J = 8$ Hz, 1 H), 8.06 (d, $J = 8$ Hz, 1 H), 7.75 (s, 2 H), 7.10 (d, $J = 8$ Hz, 2 H), 7.02 (d, $J = 8$ Hz, 2 H), 4.07 (t, $J = 6.5$ Hz, 2 H), 1.80–1.70 (m, 2 H), 1.50–1.20 (m, 18 H), 0.90 (t, $J = 6.5$ Hz, 3 H)

Compound 7. A 1.6 M solution of MeLi in hexane (6.8 mL, 10.88 mmol) was slowly added to a degassed solution of **2** (3.0 g, 6.8 mmol) in dry ether (60 mL) at 0 °C. The resulting dark red solution was stirred for 3 h, then hydrolyzed with water. CH_2Cl_2 was added and the bright yellow organic layer decanted. The aqueous layer was extracted with CH_2Cl_2 (3X) and the combined organic layers were thereafter re-aromatized by addition of MnO_2 (23 g), dried ($MgSO_4$) and filtered; the filtrate was then evaporated to dryness. Column chromatography (SiO_2, CH_2Cl_2–MeOH 97:3) gave **7** (2.73 g, 74%) as a pale yellow glassy product. ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 8.38$ (d, $J = 8$ Hz, 2 H), 8.26 (d, $J = 8$ Hz, 1 H), 8.14 (d, $J = 8$ Hz, 1 H), 8.07 (d, $J = 8$ Hz, 1 H), 7.73 (s, 2 H), 7.52 (d, $J = 8$ Hz, 1 H), 7.04 (d, $J = 8$ Hz, 2 H), 4.06 (t, $J = 6.5$ Hz, 2 H), 2.98 (s, 3 H), 1.28 (m, 18 H), 0.89 (t, $J = 6$ Hz, 3 H). ^{13}C-NMR (50 MHz, $CDCl_3$): $\delta = 160.33$, 159.16, 156.50, 145.46, 136.58, 136.05, 131.74, 128.98, 127.07, 126.87, 125.48, 123.27, 119.28, 114.47, 67.83, 31.80, 30.17, 29.48, 29.31, 29.25, 29.15, 25.93, 25.74, 22.58, 14.02. Anal. calcd for $C_{31}H_{38}N_2O$: C 81.90, H 8.42, N 6.16; found: C 81.57, H 8.42, N 6.25.

Compound Phen-3PV. DEAD (69 µL, 0.44 mmol) was added to a stirred solution of **6** (184 mg, 0.34 mmol), 3PV (280 mg. 0.32 mmol) and PPh_3 (116 mg, 0.44 mmol), in dry THF (4 mL) at 0 °C under Ar. The resulting mixture was stirred at 0 °C for 1 h, then refluxed for 3 days. After cooling, the mixture was evaporated to dryness and column chromatography (SiO_2, CH_2Cl_2) gave Phen-3PV (320 mg, 71%) as a yellow solid (mp 129 °C). ^{1}H-NMR (400 MHz, CD_2Cl_2): $\delta = 8.44$ (d, $J = 8$ Hz, 2 H), 8.41 (d, $J = 8$ Hz, 2 H), 8.30 (d, $J = 8$ Hz, 1 H), 8.29 (d, $J = 8$ Hz, 1 H), 8.11 (d, $J = 8$ Hz, 1 H), 8.10 (d, $J = 8$ Hz, 1 H), 7.78 (s, 2 H), 7.61 (d, $J = 8$ Hz, 2 H), 7.53 (AB, $J = 8$ Hz, 4 H), 7.51 (d, $J = 8$ Hz, 2 H), 7.23 (d, $J = 8$ Hz, 2 H), 7.18 (s, 2 H), 7.11 (d, $J = 8$ Hz, 2 H), 7.03 (AB, $J = 16.5$ Hz, 2 H), 6.73 (s, 2 H), 5.21 (s, 2 H), 4.08 (t, $J = 6.5$ Hz, 2 H), 4.02 (t, $J = 6.5$ Hz, 4 H), 3.93 (t, $J = 6.5$ Hz, 2 H), 1.87 (m, 6 H), 1.82 (m, 2 H), 1.50–1.20 (m, 72 H), 0.90 (t, $J = 6.5$ Hz, 12 H). ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 160.40$, 159.95, 156.22, 156.02, 153.21, 145.89, 138.25, 136.97, 136.67, 136.61, 136.29, 136.07, 132.43, 132.34, 131.79, 128.92, 128.85, 128.74, 128.37, 127.81, 127.39, 127.14, 126.78, 126.58, 125.41, 114.96, 114.61, 105.06, 73.42, 69.67, 69.03, 67.97, 31.85, 30.30, 29.68, 29.60, 29.37, 29.31, 26.06, 26.00, 22.61, 14.05. Anal. calcd for $C_{95}H_{130}N_2O_5.H_2O$: C 81.61, H 9.52, N 2.00; found C 81.90, H 9.55, N 1.98.

Compound Phen-4PV. Phen-4PV was synthesized as described for Phen-3PV from **6** (198 mg, 0.37 mmol), 4PV (300 mg, 0.31 mmol), PPh_3 (113 mg, 0.43 mmol) and DEAD (68 µL, 0.43 mmol) in dry THF (4 mL). Column chromatography (SiO_2, CH_2Cl_2) gave Phen-4PV (295 mg, 65%) as a yellow solid (mp 156 °C). ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 8.44$ (d, $J = 8$ Hz, 2 H), 8.41 (d, $J = 8$ Hz, 2 H), 8.30 (d, $J = 8$ Hz, 1 H), 8.29 (d, $J = 8$ Hz, 1 H), 8.11 (d, $J = 8$ Hz, 1 H), 8.10 (d, $J = 8$ Hz, 1 H), 7.77 (s, 2 H), 7.51 (m, 16 H), 7.23 (d, $J = 8$ Hz, 2 H), 7.16 (s, 2 H), 7.14 (s, 2 H), 7.11 (d, $J = 8$ Hz, 2 H), 7.03 (AB, $J = 16.5$ Hz, 2 H), 6.73 (s, 2 H), 5.21 (s, 2 H), 4.08 (t, $J = 6.5$ Hz, 2 H), 4.02 (t, $J = 6.5$ Hz, 4 H), 3.93 (t, $J = 6.5$ Hz, 2 H), 1.87 (m, 6 H), 1.82 (m, 2 H), 1.50–1.20 (m, 72 H), 0.90 (t, $J = 6.5$ Hz, 12 H). ^{13}C-NMR (50 MHz, $CDCl_3$): $\delta = 160.52$, 160.49, 156.44, 153.31, 146.04, 138.40, 137.16, 136.78, 136.62, 136.49, 136.24, 132.50, 129.03, 128.94, 128.54, 128.13, 127.95, 127.49, 127.24, 126.82, 126.71, 125.64, 125.54, 119.31, 115.11, 114.73, 105.22, 77.19, 73.52, 69.86, 69.18, 68.12, 31.91, 30.33, 29.64, 29.43, 26.11, 22.67, 14.09. Anal. calcd for $C_{103}H_{136}N_2O_5$: C 83.46, H 9.25, N 1.89; found C 83.29, H 9.19, N 1.85.

Compound Cu^+(Phen-3PV)$_2$. $Cu(CH_3CN)_4{\cdot}BF_4$ (33 mg, 0.10 mmol) was added to a solution of Phen-3PV (240 mg, 0.17 mmol) in CH_2Cl_2 (5 mL) at room temperature under Ar. The resulting dark red solution was stirred for 20 min and evaporated to dryness. Column chromatography (Al_2O_3, CH_2Cl_2 to CH_2Cl_2–MeOH 99:1) gave Cu^+(Phen-3PV)$_2$ (230 mg, 90%) as a red-brown glassy product. ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 8.47$ (d, $J = 8$ Hz, 2 H), 8.45 (d, $J = 8$ Hz, 2 H), 7.96 (s, 4 H), 7.87 (d, $J = 8$ Hz, 2 H), 7.85 (d, $J = 8$ Hz, 2 H), 7.60–7.34 (m, 24 H), 7.17 (s, 4 H), 7.02 (AB, $J = 16.5$ Hz, 4 H), 6.73 (s, 4 H), 6.16 (d, $J = 8$ Hz, 4 H), 6.02 (d, $J = 5$ Hz, 4 H), 5.31 (s, 4 H), 4.08 (t, $J = 6.5$ Hz, 4 H), 4.02 (t, $J = 6.5$ Hz, 8H), 3.93 (t, $J = 6.5$ Hz, 4 H), 1.87 (m, 12 H), 1.82 (m, 4 H), 1.50–1.20 (m, 144 H), 0.90 (t, $J = 6.5$ Hz, 24 H). ^{13}C-NMR (50 MHz, $CDCl_3$): $\delta = 159.62$, 159.15, 158.31, 158.22, 153.25, 143.39, 138.31, 137.16, 136.84, 136.27, 135.78, 132.44, 131.35, 130.89, 129.07, 128.83, 128.59, 127.79, 127.15, 126.86, 126.66, 124.41, 113.36, 112.93, 105.12, 73.48, 69.45, 69.11, 67.83, 31.87, 30.31, 29.63, 29.40, 29.32, 28.97, 26.09, 22.64, 14.07. FAB-MS: $m/z = 2823.0$ ($[M - BF_4]^+$ (calcd for $C_{190}H_{260}N_4O_{10}Cu$: 2823.7). Anal. calcd for $C_{190}H_{260}N_4O_{10}CuBF_4$: C 78.41, H 9.00, N 1.92; found C 78.33, H 8.96, N 1.88.

Compound Cu^+(Phen-4PV)$_2$. Cu^+(Phen-4PV)$_2$ was synthesized as described for Cu^+(Phen-3PV)$_2$ from Phen-4PV (135 mg, 0.09 mmol) and $Cu(CH_3CN)_4{\cdot}BF_4$ (18 mg, 0.05 mmol) in CH_2Cl_2 (5 mL). Column chromatography (Al_2O_3, CH_2Cl_2 to CH_2Cl_2–MeOH 99:1) gave Cu^+(Phen-4PV)$_2$ (130 mg, 90%) as a red-brown glassy product. ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 8.47$ (d, $J = 8$ Hz, 2 H), 8.45 (d, $J = 8$ Hz, 2 H), 7.96 (s, 4 H), 7.87 (d, $J = 8$ Hz, 2 H), 7.85 (d, $J = 8$ Hz, 2 H), 7.60–7.34 (m, 32 H), 7.17 (s, 4 H), 7.13 (s, 4 H), 7.02 (AB, $J = 16.5$ Hz, 4 H), 6.73 (s, 4 H), 6.16 (d, $J = 8$ Hz, 4 H), 6.02 (d, $J = 8$ Hz, 4 H), 5.31 (s, 4 H), 4.08 (t, $J = 6.5$ Hz, 4 H), 4.02 (t, $J = 6.5$ Hz, 8H), 3.93 (t, $J = 6.5$ Hz, 4 H), 1.87 (m, 12 H), 1.82 (m, 4 H), 1.50-1.20 (m, 144 H), 0.90 (t, $J = 6.5$ Hz, 24 H). ^{13}C-NMR (50 MHz, $CDCl_3$): $\delta = 159.69$, 159.25, 156.44, 153.31, 143.48, 137.26, 136.90, 136.43, 135.79, 132.49, 131.41, 129.04, 128.86, 128.70, 128.28, 127.95, 127.81, 127.23, 126.85, 126.72, 126.01, 124.50, 124.47, 113.47, 113.00, 105.25, 73.53, 69.58, 69.19, 67.90, 31.90, 30.33, 29.64, 29.43, 29.35, 29.01, 26.12, 22.67, 14.09. Anal. calcd for $C_{206}H_{272}N_4O_{10}CuBF_4$: C 79.44, H 8.80, N 1.80; found C 79.40, H 8.77, N 1.73.

Compound Cu$^+$(3)$_2$. Cu$^+$(**3**)$_2$ was synthsized as described for Cu$^+$(Phen-3PV)$_2$ from **3** (50 mg, 0.07 mmol) and $Cu(CH_3CN)_4{\cdot}BF_4$ (13 mg, 0.04 mmol) in CH_2Cl_2 (10 mL). Column chromatography (Al_2O_3, CH_2Cl_2–MeOH 9:1) gave Cu$^+$(**3**)$_2$ (130 mg, 60%) as a dark red solid (mp 78 °C). ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 8.45$ (d, $J = 8$ Hz, 4 H), 7.99 (s, 4 H), 7.85 (d, $J = 8$ Hz, 4 H), 7.45 (d, $J = 8$ Hz, 8 H), 6.05 (d, $J = 8$ Hz, 8 H), 3.53 (t, $J = 6.5$ Hz, 8 H), 1.77 (m, 8 H), 1.35 (m, 72 H), 0.90 (t, $J = 6.5$ Hz, 12 H). ^{13}C-NMR (50 MHz, $CDCl_3$): $\delta = 160.18$, 156.83, 143.87, 137.18, 131.29, 129.64, 128.19, 126.29, 124.65, 113.22, 68.25, 32.31, 30.02, 29.75, 29.35, 26.41, 23.08, 14.27. Anal. calcd for $C_{96}H_{128}N_4O_4CuBF_4$: C 74.27, H 8.31, N 3.61; found C 74.41, H 8.00, N 3.80.

Compound Cu$^+$(7)$_2$. Cu$^+$(**7**)$_2$ was synthesized as described for Cu$^+$(Phen-3PV)$_2$ from **7** (100 mg, 0.21 mmol) and $Cu(CH_3CN)_4{\cdot}BF_4$ (41 mg, 0.13 mmol). Column chromatography (Al_2O_3, CH_2Cl_2–MeOH 92:8) gave Cu$^+$(**7**)$_2$ (100 mg, 72%) as a dark red glassy product. ^{1}H-NMR (200 MHz, CD_2Cl_2): $\delta = 8.45$ (d, $J = 8$ Hz, 2 H), 8.43 (d, $J = 8$ Hz, 2 H), 8.00 (s, 4 H), 7.85 (d, $J = 8$ Hz, 2 H), 7.75 (d, $J = 8$ Hz, 2 H), 7.15 (d, $J = 8$ Hz, 4 H), 5.65 (d, $J = 8$ Hz, 4 H), 3.48 (t, $J = 6.5$ Hz, 4 H), 2.60 (s, 3 H), 1.68 (m, 4 H), 1.38 (m, 36 H), 0.85 (t, $J = 6.5$ Hz, 6 H). ^{13}C-NMR (50 MHz, CD_2Cl_2): $\delta = 159.73$, 157.72, 157.59, 143.70, 143.61, 137.33, 137.10, 131.83, 129.06, 127.99, 127.95, 126.31, 126.06, 125.90, 124.46, 112.97, 68.03, 32.25, 30.00, 29.76, 29.70, 29.35, 26.51, 26.41, 23.03, 14.22. Anal. calcd for $C_{62}H_{76}N_4O_2CuBF_4$: C 70.28, H 7.23, N 5.29; found C 70.72, H 7.30, N 5.30.

Electrochemistry

The electrochemical studies were carried out in CH_2Cl_2 (Fluka spectroscopic grade used without further purification) containing 0.1 M Bu_4NPF_6 (Merck electrochemical grade) as supporting electrolyte. A classical three-electrode cell was connected to a computerized electrochemical Autolab (Eco Chemie B.V. Utrecht, Holland) device driven by GPSE software running on a personal computer. The working electrode was a glassy carbon disk (3 mm in diameter), the auxiliary electrode a platinum wire and the reference electrode an aqueous Ag/AgCl reference electrode. All potentials are given *versus* Fc/Fc$^+$ used as internal standard.

Photophysical measurements

The solvents used for spectroscopic investigations were CH_2Cl_2 and CH_3OH (Carlo Erba, spectrofluorimetric grade). The samples were placed in fluorimetric 1 cm path cuvettes and, when necessary, purged of oxygen by bubbling argon. Absorption spectra were recorded with a Perkin–Elmer λ45 spectrophotometer. Uncorrected emission spectra were obtained with a Spex Fluorolog II spectrofluorimeter (continuous Xe lamp, 150 W), equipped with a Hamamatsu R-928 photomultiplier tube. The procedure used to correct emission spectra was reported earlier.[43] Fluorescence quantum yields for degassed samples in CH_2Cl_2 solvent were obtained from spectra on an energy scale (cm^{-1}) according to the approach described by Demas and Crosby[49] using quinine sulfate in 1 N H_2SO_4 ($\Phi = 0.546$)[50] and air-equilibrated $[Os(phen)_3]^{2+}$ in acetonitrile ($\Phi_{em} = 0.005$)[51] as standards. For steady-state and time-resolved luminescence experiments at 77 K we employed a 1:1 (v/v) mixture of CH_2Cl_2 and MeOH, that was found to yield good quality transparent glasses. In this case, the samples were placed in pyrex capillary tubes (2 mm diameter) immersed in liquid nitrogen contained in a home-made quartz dewar. Emission lifetimes in the ns–μs time scale were determined with an IBH single photon counting spectrometer equipped with a thyratron gated nitrogen lamp working in the 4–40 KHz range ($\lambda_{exc} = 337$ nm, 0.5 ns time resolution); the detector was a red-sensitive (185–850 nm) Hamamatsu R-3237-01 photomultiplier. The uncertainties are ±2 nm, ±20% and ±5%, for emission maxima, emission intensities and quantum yields, and excited state lifetimes, respectively.

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