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Porphyrin-Appended Europium(III) Bis(phthalocyaninato) Complexes: Synthesis, Characterization, and Photophysical Properties

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Abstract: Mixed cyclization of 3-mono-, 4-mono-, or 4,5-di(porphyrinated) phthalonitrile compounds **2**, **3**, or **6** and unsubstituted phthalonitrile with the half-sandwich complex [Eu^{III}(acac)(Pc)] (Pc = phthalocyaninate, acac = acetylacetonate) as the template in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in *n*-pentanol afforded novel porphyrin-appended europium(III) bis(phthalocyaninato) complexes **7**–**9** in 30–40 % yield. These mixed tetrapyrrole triads and tetrad were spectroscopically and electrochemically characterized and their photophysical properties were also investigated with steady-state and transient spectroscopic methods. It has been found that the fluorescence of the porphyrin moiety is quenched effectively by the double-decker unit through an intramolecular photoinduced electron-transfer process, which takes place in several hundred femtoseconds, while the recombination of the charge-separated state occurs in several picoseconds. By using different phthalocyanines containing different numbers of porphyrin substituents at the peripheral or nonperipheral position(s) of the ligand, while the other unsubstituted phthalocyanine remains unchanged in these double-deckers, the effects of the number and the position of the porphyrin substituents on these photophysical processes were also examined.

Keywords: electron transfer · europium · phthalocyanines · porphyrinoids · sandwich complexes

Introduction

To have a better understanding of and, as the final target, to mimic the natural photosynthetic process, much effort has been devoted to the study of various photosynthesis model compounds, including their synthesis, structure, and in particular photophysical properties involving electron- and/or energy-transfer processes.[1] Apart from the biological relevance, these compounds have also attracted further research interest due to their many potential applications in solar energy transfer[2] and molecular-scale optoelectronics and photonics.[3] It is now well known that the key step in photosynthesis is the chain electron transfer across the membrane that happens in the reaction center (RC). The RC contains a bacteriochlorophyll dimer with a slipped cofacial orientation, called a "special pair", as the primary donor for the electron transfer, which leads to a steady charge-separated state.[4]

Owing to a molecular structure which is closely related to that of bacteriochlorophyll in the RC, porphyrin derivatives, including their most important artificial analogues, phthalocyanines, have been among the most attractive artificial photosynthetic systems.[5] In order to extend the absorption region, phthalocyanine derivatives have also been conjugated with porphyrins by covalent linkages or supramolecular interactions, thereby forming heteroarrays of tetrapyrrole derivatives.[6,7] Photophysical studies of these systems have revealed that the photoinduced electron- and energy-transfer processes between the porphyrin and phthalocyanine

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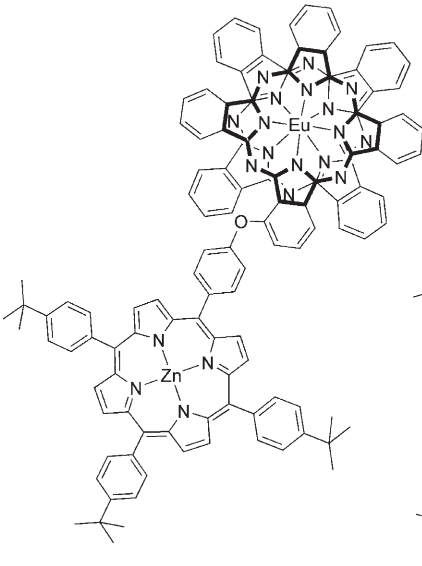
chromophores are very efficient and can be altered by changing the structure and the environment.[7]

Sandwich-type bis(porphyrinato), as well as the bis(phthalocyaninato), metal complexes have been extensively studied.[8] The impetus comes not only from the intriguing structures and properties of the molecules but also from their potential applications in molecular electronic, photonic, and ionoelectronic devices. Due to the close face-to-face proximity of the tetrapyrrole ligands, these compounds also resemble the special pair and can therefore serve as synthetic structure and spectroscopic models. However, the photophysical properties of sandwich-type bis(tetrapyrrole) metal complexes have not been well studied. In the present paper, we describe in detail the synthesis and the spectroscopic and, in particular, the photophysical characteristics of three novel europium(III) bis(phthalocyaninato) complexes appended with one or two zinc(II) porphyrin unit(s) synthesized from porphyrin-containing phthalonitriles (compounds **1**–**6**, Scheme 1).

It is worth noting that the electronic absorption properties of phthalocyanine derivatives can be tuned by changing the type, number, and positions of the substituents of the macrocycle ligand.[9] However, to the best of our knowledge, there has been no report in which the influence of the substituents of the phthalocyanine ligand on the photophysical properties of the corresponding phthalocyanine compounds has been studied. For this purpose, novel porphyrin-appended europium(III) bis(phthalocyaninato) complexes **7**–**9** have been designed, prepared, and characterized. By using different phthalocyanines containing different numbers of porphyrin substituents at the peripheral or nonperipheral position(s) of the ligand, while the other unsubstituted phthalocyanine remains unchanged in these double-deckers, the effects of the number and in particular the position of the porphyrin substituent(s) on these photophysical processes were also examined. This represents the first trial toward understanding the effects of substituents at the phthalocyanine ligand on the photoinduced electron- and/or energy-transfer processes based on bis(phthalocyaninato) rare earth systems.



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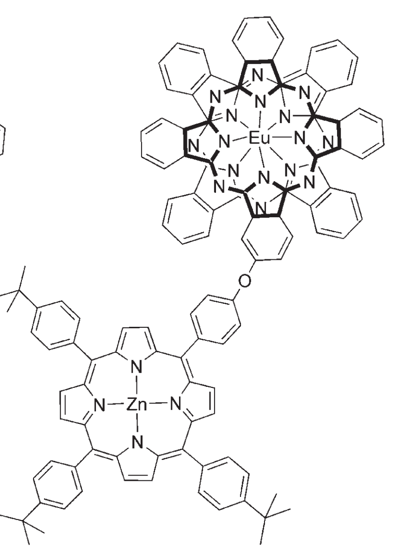

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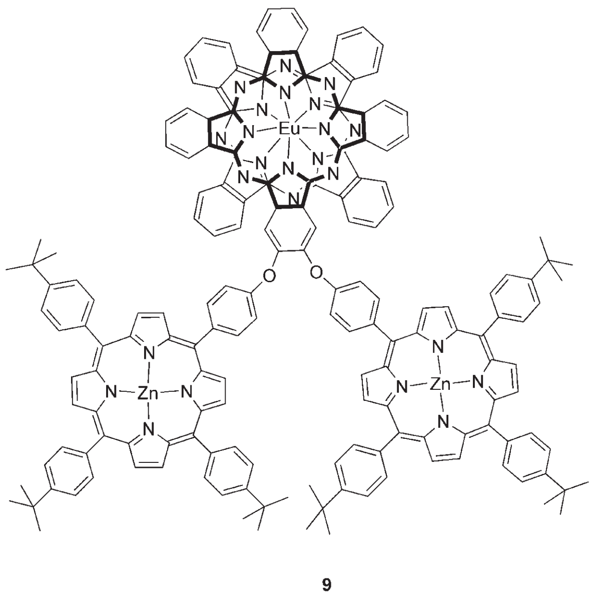

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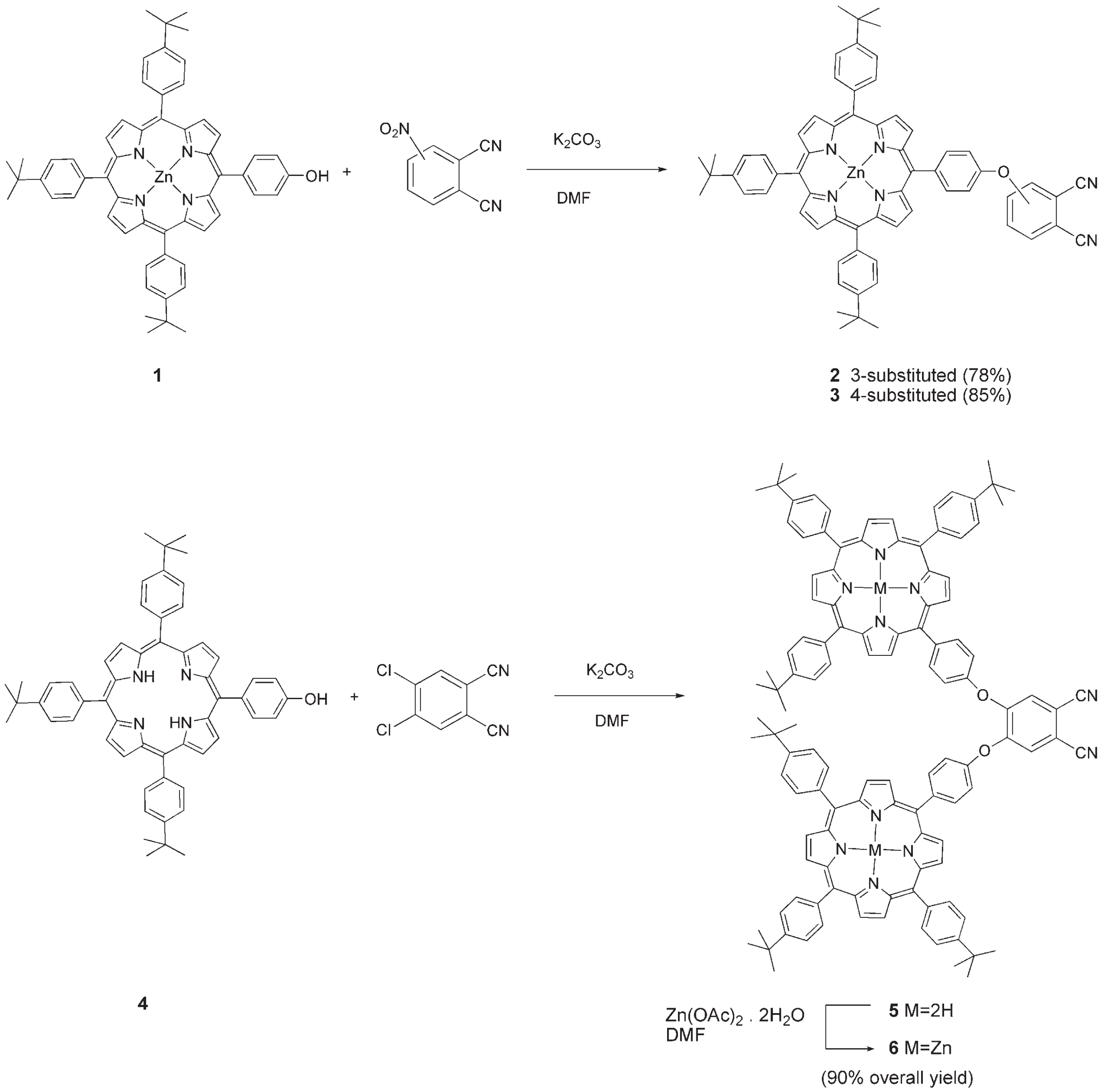
Results and Discussion

Synthesis: The synthesis of the porphyrin-containing phthalonitriles is shown in Scheme 1. Treatment of zinc(II) 5,10,15-tris(4-*tert*-butylphenyl)-20-(4-hydroxyphenyl)porphyrin ([Zn(TriBPPH)], **1**)[10] with 3- or 4-nitrophthalonitrile and K_2CO_3 in DMF gave the corresponding substituted product **2** or **3** in good yield. The 4-substituted analogue **3** was prepared previously by Maillard and co-workers by



Scheme 1. Schematic synthesis of the porphyrin-containing phthalonitriles.

using the same methodology.[11] Owing to lower solubility, the 4,5-bis(porphyrinyl)phthalonitrile **6** was prepared from the metal-free porphyrin **4**. Treatment of this compound with 4,5-dichlorophthalonitrile and K_2CO_3 in DMF at 90 °C gave the disubstituted product **5**,[12] which underwent metallation with $Zn(OAc)_2{\cdot}2H_2O$ to afford **6**.[13] The porphyrin-containing phthalonitriles **2**, **3**, and **6** were then subjected to a one-pot mixed cyclization with unsubstituted phthalonitrile and with $[Eu^{III}(acac)(Pc)]$ as the template in the presence of DBU in refluxing *n*-pentanol.[14,15] As expected, these reactions led to the formation of a mixture of cyclized products from which the desired products **7**–**9** could be isolated in reasonably good yield by silica-gel and biobead column chromatography.

Satisfactory elemental analysis results were obtained for all of the newly prepared heterotetrapyrrole arrays **7**–**9**. The compounds were further characterized by MALDI-TOF mass spectrometric and NMR spectroscopic methods. The MALDI-TOF mass spectra of these compounds clearly showed intense signals for either the molecular ion $[M]^+$ or the protonated molecular ion $[M+1]^+$. The isotopic pattern closely resembled the simulated one, as exemplified by the spectrum of **7** given in Figure S1 (see the Supporting Information).

Spectroscopic characteristics: The electronic absorption data of the heteroarrays **7**–**9** were measured in $CHCl_3$ and are compiled in Table 1. The electronic absorption spectra of all the arrays are very similar to the sum of the spectra of an

Table 1. Electronic absorption data for the heterotetrapyrrole arrays **7**–**9** and the reference compounds in $CHCl_3$.

Compound	λ_{max} [nm] (log ε)										
[Zn(TriBPPH)]			400	421		548	588				
			(4.75)	(5.91)		(4.49)	(3.87)				
$[Eu(Pc)_2]$	321	344			461		587	604	671	907	1599
	(5.18)	(4.99)			(4.57)		(4.52)	(4.61)	(5.33)	(3.44)	(5.27)
7	321	343	400	421	455	549	592	607	675	909	1618
	(5.18)	(5.01)	(4.89)	(5.87)	(4.57)	(4.62)	(4.65)	(4.68)	(5.29)	(3.70)	(4.23)
8	321	343	400	421	455	548	587	604	672	909	1602
	(5.20)	(5.04)	(4.89)	(5.90)	(4.59)	(4.61)	(4.59)	(4.63)	(5.31)	(3.73)	(4.21)
9	320	344	401	422	466	549	587	604	672	909	1595
	(5.24)	(5.10)	(5.18)	(6.08)	(4.61)	(4.86)	(4.67)	(4.65)	(5.35)	(3.49)	(3.94)

equimolar (for **7** and **8**) or 1:2 (for **9**) mixture of $[Eu(Pc)_2]$ and **1**, a result indicating the absence of a strong electronic interaction between the two components. For example, in the spectrum of **8** (Figure 1), the strong band at 421 nm with a weak shoulder at the higher energy side (400 nm) is the porphyrin Soret band and the weak bands at 548 and 587 nm are attributed to the porphyrin Q bands. The remaining absorptions are all due to the electronic transitions of the bis(phthalocyaninato) europium(III) component. The broad band at 321 nm with a shoulder at 343 nm is attributed to the phthalocyanine Soret band. The relatively intense absorption at 672 nm with a vibronic band at 604 nm is due to the phthalocyanine Q band. The three absorptions at 455, 909, and 1602 nm are all characteristic $Pc^{\bullet-}$-related bands of bis(phthalocyaninato) europium(III) complexes. It is noteworthy that the peak at 455 nm, which is due to the electron transition involving the semioccupied orbital of the double-decker, is blue shifted relative to that of $[Eu(Pc)_2]$ at 461 nm. This blue shift is believed to be due to the phenyloxy substituents.[16]

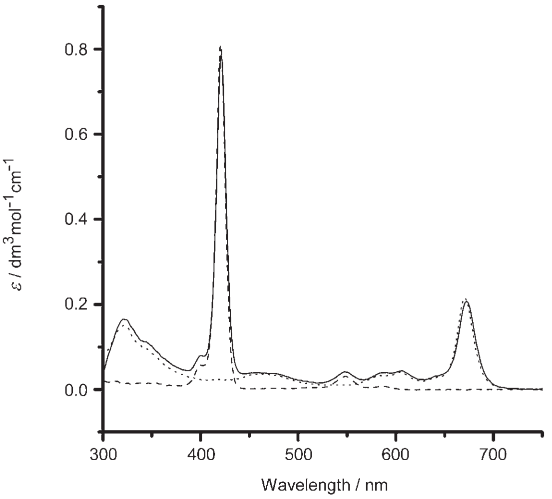


Figure 1. The electronic absorption spectra of [Eu(Pc){Pc(β-Zn(TriBPP)}] (**8**; ——) in comparison with those of $[Eu(Pc)_2]$ (•••••) and [Zn(TriBPPH)] (-----) in $CHCl_3$.

With a higher porphyrin content, compound **9** showed stronger bands for all of the porphyrin-related absorptions. Generally speaking, the Q bands for a double-decker with a porphyrin moiety at the nonperipheral α position (that is, **7**) are slightly red shifted compared with double-deckers with peripheral porphyrin unit(s) (that is, **8** and **9**).[14]

It is well known that single-hole-containing neutral bis(phthalocyaninato) rare earth(III) complexes can be easily converted into the corresponding reduced form by using either hydrazine hydrate or $NaBH_4$ as the reducing agent.[17] Upon addition of hydrazine hydrate into a $CHCl_3$/MeOH 3:1 solution of $[Eu(Pc)_2]$, all of the three $Pc^{\bullet-}$ absorption bands at 461, 907, and 1599 nm disappeared. The main Pc Soret band was red shifted to 333 nm and two new Q bands appeared at 635 and 681 nm, all attributable to the anionic double-decker $[Eu^{III}(Pc^{2-})(Pc^{2-})]^-$. Under similar conditions, the absorption spectrum of **1** was also significantly changed as a result of the formation of axially coordinated adduct $[Zn(TriBPPH)(NH_2NH_2)]$.[18] As shown in Table 2, the electronic absorption data of the heteroarrays **7**–**9** in the presence of hydrazine hydrate can be ascribed to the sum of those arising from the components $[Eu(Pc)_2]^-$ and $[Zn(TriBPPH)(NH_2NH_2)]$.

The presence of an unpaired electron in the double-decker component in **7**–**9** was further supported by IR spectroscopy. An intense IR band at 1318 or 1319 cm^{-1} was observed for these complexes; this band is a marker for the phthalocyanine radical anion $Pc^{\bullet-}$.[19]

Table 2. Electronic absorption data for $[Zn(TriBPPH)(NH_2NH_2)]$, $[Eu(Pc)_2]^-$, and reduced heterotetrapyrrole arrays **7**–**9** in $CHCl_3$/MeOH 3:1.

Compound									
$[Zn(TriBPPH)(NH_2NH_2)]$				407	428	564	604	631	683
				(4.80)	(5.91)	(4.41)	(4.28)	(5.34)	(4.84)
$[Eu(Pc)_2]^-$	283	333	359				583	635	681
	(4.96)	(5.28)	(4.81)				(4.45)	(5.33)	(4.82)
[Eu(Pc){Pc{α-Zn(TriBPP)}-(NH_2NH_2)}]$^-$	290	332	360	408	429	566	609	632	682
	(5.01)	(5.27)	(4.86)	(4.89)	(5.87)	(4.55)	(4.81)	(5.35)	(4.84)
[Eu(Pc){Pc{β-Zn(TriBPP)}-(NH_2NH_2)}]$^-$	284	332	362	407	428	566	603	632	683
	(5.03)	(5.28)	(4.87)	(4.89)	(5.90)	(4.56)	(4.77)	(5.41)	(4.92)
[Eu(Pc){Pc{β-Zn(TriBPP)}$_2$-$(NH_2NH_2)_2$}]$^-$	284	333	360	408	429	564	603	631	683
	(5.21)	(5.39)	(5.06)	(5.21)	(6.08)	(4.83)	(4.94)	(5.34)	(4.84)

The ^{1}H NMR spectra of **7**–**9** in $CDCl_3$ showed only the signals that could be ascribed to the porphyrin unit. Owing to the presence of an unpaired electron, signals due to the double-decker moiety were not seen. However, upon addition of hydrazine hydrate, which reduced the double-deckers to the corresponding diamagnetic dianions, these signals emerged as two sets of multiplets corresponding to the phthalocyanine α and β ring protons. If compound **9** is taken as an example, the spectrum in deuterated dimethylsulfoxide ([D$_6$]DMSO) in the presence of approximately 1% hydrazine hydrate showed these signals at $\delta = 10.80$–11.26 (Pc-Hα) and 8.91–9.29 ppm (Pc-Hβ).[20] The latter signals overlapped with those of the porphyrin protons. The OC_6H_4 phenylene protons resonated as two doublets at $\delta = 9.88$ and 9.41 ppm, while the tBuC_6H_4 phenylene protons appeared as two multiplets at $\delta = 8.20$–8.28 and 7.82–7.90 ppm. Their correlations were confirmed by the 2D COSY spectrum. The *t*Bu groups resonated as two singlets at $\delta = 1.78$ and 1.61 ppm in a 2:1 ratio. The spectra of **7** and **8** have similar spectral characteristics and can be similarly assigned (see the Experimental Section). It is worth noting that, in line with the phenomenon found for the porphyrin–phthalocyanine dyads,[21] the integral value for the aromatic protons of the porphyrin ligand(s) in heterotriads **7** and **8** and heterotetrad **9** is a bit smaller than expected according to that of the nonaromatic *t*Bu protons of the porphyrin ligand(s).

Electrochemical properties: The electrochemical behavior of all the newly prepared tetrapyrrole arrays **7**–**9** together with **1** and [Eu(Pc)$_2$][22] was investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in CH_2Cl_2. The heteroarrays displayed up to four oxidations and up to six reductions within the electrochemical window of CH_2Cl_2 under ambient conditions. All these processes could be attributed to successive removal from, or addition of electron(s) to, the tetrapyrrole ligand based orbitals. The half-wave redox potential values versus the saturated calomel electrode (SCE) are summarized in Table 3. Representative differential pulse voltammograms for **7** are displayed and compared with those of **1** and [Eu(Pc)$_2$] in Figure S2 in the Supporting Information. A direct comparison of their electrochemical data (Table 3) helped to reveal the origin of the various redox processes of **7**. Accordingly, the redox couples at +1.30, +1.03, +0.73, and −0.88 V for **7** could be attributed to the porphyrin component, while the couples at +0.54, +0.13, −1.10, and −1.40 V were assigned to the double-decker unit. The two extra reduction couples at −1.57 and −1.74 V shown in the DPV for **7** should have contributions from both the porphyrin and the bis(phthalocyaninato) europium(III) moieties. Similar assignments could also be made for compounds **8** and **9**.

Photophysical properties: The fluorescence measurements indicated that the emission of the porphyrin chromophore in compounds **7**–**9** was completely quenched by the double-decker component. The results were in line with studies of other covalently linked mixed porphyrin–phthalocyanine systems, which normally exhibit efficient photoinduced energy and/or electron transfer between the two chromophores.[7] On the basis of the good spectral overlap between the emission of [Zn(TriBPPH)] and the absorptions of [Eu(Pc)$_2$], there is a possibility of a photoinduced intramolecular singlet–singlet energy-transfer process from the excited porphyrin chromophore to the bis(phthalocyaninato) europium(III) unit in heteroarrays **7**–**9**. On the other hand, photoinduced electron transfer from the porphyrin chromophore to the phthalocyanine double-decker for **7**–**9** is also a thermodynamically favorable process ($\Delta G = -0.11$ V), as shown by the calculation according to the Rehm–Weller equation [Eq. (1)],[23] where $E_{\rm ox}$ and $E_{\rm red}$ are the oxidation potential of [Zn(TriBPPH)] and reduction potential of [Eu(Pc)$_2$], respectively; $E_{\rm S}$ is the first excited singlet-state energy; $e_{\rm o}$ is the electronic charge; r is the center-to-center distance between the ions (which is approximately 12 Å for **7**–**9** based on molecular modeling); $\varepsilon_{\rm S}$ is the static dielectric constant of the medium (which is 6.9 for tetrahydrofuran (THF)); and S is the difference between the energies of the ion-pair product in the polar solvent in which the $E_{\rm ox}$ and $E_{\rm red}$ values are measured and in another less polar solvent in which the electron-transfer rate constants are measured.[24]

$$\Delta G = E_{\rm ox} - E_{\rm red} - E_{\rm S} - e_{\rm o}^2/r\varepsilon_{\rm S} + S$$

In order to identify the responsible process for the fluorescence quenching of compounds **7**–**9**, the transient absorption spectra of these compounds in methyltetrahydrofuran (MTHF) were recorded. For the purpose of comparative studies, the transient absorption spectrum of the model compound **1** was also measured. The transient absorption spectra of **7**–**9**, on the nanosecond scale, were found to show no meaningful signals in the UV/Vis region, a result indicating that no photoinduced processes occur on this timescale. By contrast, absorption of the zinc porphyrin triplet state in the nanosecond transient absorption spectrum of **1** was detected with a long lifetime. The quenching of this long-lived triplet species in **7**–**9** indicates that the photoinduced process between the porphyrin chromophore and [Eu(Pc)$_2$] double-decker is very quick.

The time-resolved absorption spectra of triad **7** together with the model compounds **1** and [Eu(Pc)$_2$], upon excitation by a 150 fs laser pulse at 400 nm, were recorded and are shown in Figure 2. It can be seen in the spectrum of **1** that a broad

Table 3. Half-wave redox potentials of heterotetrapyrrole arrays **7**–**9** (V versus the SCE) in CH_2Cl_2 containing 0.1 M tetrabutylammonium perchlorate recorded by DPV.

[Zn(TriBPPH)]	+1.55	+1.27	+1.02	+0.72			−0.89			−1.66	−1.88
[Eu(Pc)$_2$]	+1.59				+0.55	+0.12		−1.07	−1.29	−1.54	−1.70
7		+1.30	+1.03	+0.73	+0.54	+0.13	−0.88	−1.10	−1.40	−1.57	−1.74
8		+1.31	+1.03	+0.74	+0.55	+0.12	−0.89	−1.13	−1.45	−1.59	−1.74
9			+1.04	+0.77	+0.59	+0.16	−0.80	−1.06	−1.42		

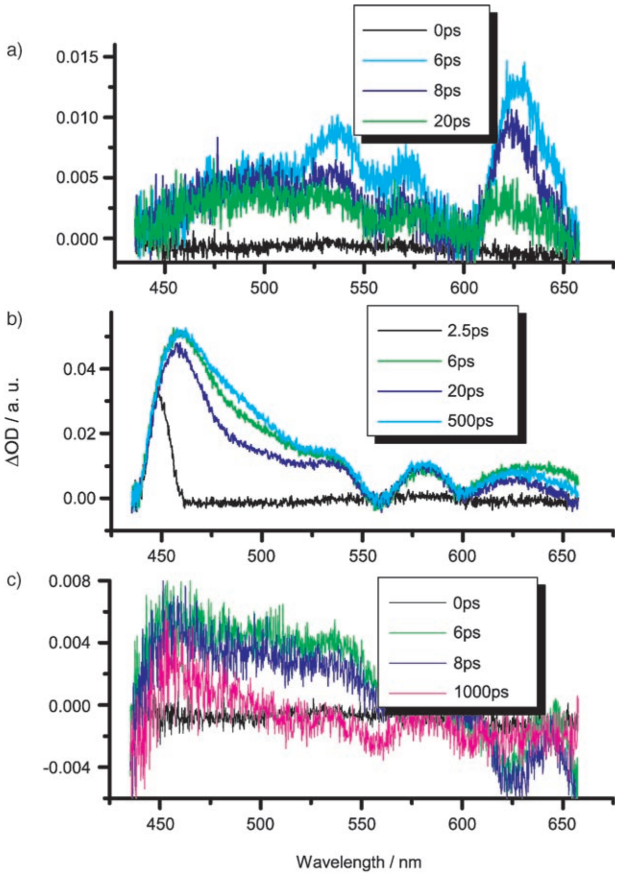


Figure 2. Time-resolved absorption spectra of a) compound **7**, b) [Zn(TriBPPH)], and c) $[Eu(Pc)_2]$ in MTHF after a 150 fs laser pulse excitation.

intense absorption appears at about 475 nm accompanied by two weak absorptions at about 530 and 630 nm, which are assigned to the absorptions of the porphyrin singlet excited states. Very *weak* and *broad* absorptions in the range of 400–575 nm were observed in the femtosecond transient absorption spectrum of $[Eu(Pc)_2]$. This, at this stage, can probably be ascribed to the triplet state of $[Eu(Pc)_2]$ because of the long-lifetime feature. As for triad **7**, an absorption peak at approximately 627 nm was observed. The intensity of this absorption was found to change with time. It increases rapidly after the excitation and reaches a maximum at about 6 ps, after which it decays quickly to the base line at about 20 ps. Spectral electrochemical measurements on $[Eu(Pc)_2]$ indicated the monoanionic nature of this absorption (see the Supporting Information). As a result, the time-dependent absorption band at 620 nm in the femtosecond absorption spectra of **7**–**9** is ascribed to the monoanion of bis(phthalocyaninato) europium, $[Eu(Pc)_2]^-$, produced by photoinduced electron transfer from the porphyrin chromophore to the double-decker one; this clearly indicates that the photoinduced electron-transfer process from the porphyrin chromophore to the bis(phthalocyninato) europium double-decker occurs in triad **7** as well as in triad **8** and tetrad **9**.[7]

Kinetic profiles of the transient absorption spectra for triad **7** are displayed Figure 3. The absorption at 475 nm, assigned to the absorption of the S1 states of the porphyrin chromophore, shows a rapid increase followed by a quick decay. Dynamic analysis of the decay profile indicates one exponential decay with a lifetime of 320 fs. This value is in good agreement with the lifetime of 1 exponential growth for the formation of absorption at 627 nm in compound **7**, which is 350 fs, according to the dynamic analysis of the increase profile of this absorption. This agreement indicates that the formation of the bis(phthalocyaninato) europium monoanion, $[Eu(Pc)_2]^-$, occurs on depletion of the singlet states of the porphyrin chromophore and thus directly suggests the very quick and efficient photoinduced electron transfer from the porphyrin chromophore to the phthalocyanine double-decker part in this compound.

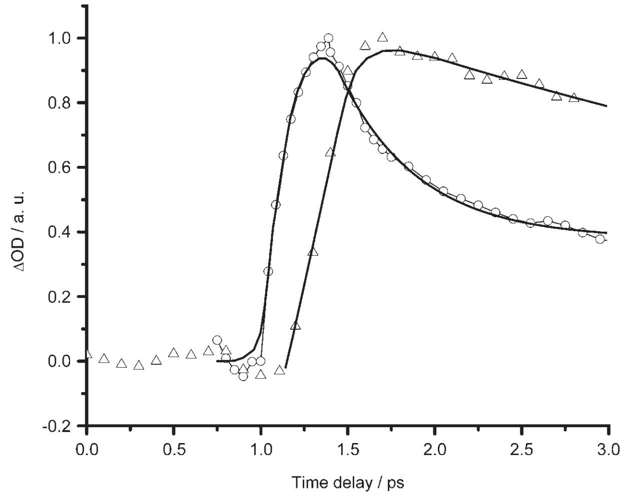


Figure 3. Kinetic profiles of the transient absorption spectra for compound **7** in THF at 470 nm (○) and 620 nm (△). The solid lines are the corresponding fitting curves.

The kinetic profile of the charge-recombination process for triad **7** is monitored by the decay of the absorption at 627 nm (Figure 4). The fitting of the decay profile gives two lifetimes, 2.5 and 30 ps, respectively, with the short lifetime dominating (95 %) the decay. We ascribe the short lifetime to the recombination process through space, while the long lifetime is assigned to the process through bonds, in accordance with the reported results on other related systems.[25]

Similar fast and efficient photoinduced electron transfer from the porphyrin chromphore to the phthalocyanine double-decker fraction was also revealed for triad **8** and tetrad **9**. The corresponding kinetic data are compiled in Table 4. However, in comparison with the β-substituted analogue **7**, the α-substituted counterpart **8** gives a slower electron transfer and recombination process due to the increased separation between the porphyrin chromophore and the $[Eu(Pc)_2]$ unit. This is in accordance with the results reported for other porphyrin–phthalocyanine dyad systems.[6b] Most interestingly, the electron transfer and recombination

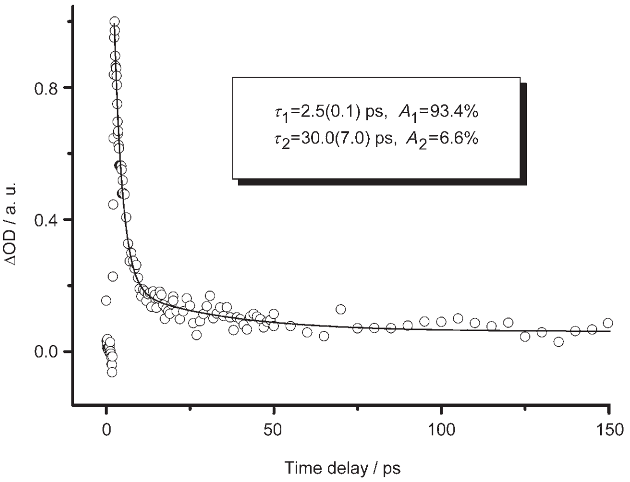


Figure 4. Kinetics of the absorption at 620 nm of compound **7** in THF after a laser pulse excitation (○). The solid line is the fitting curve. The inset shows the fitting results of the experiment data.

Table 4. Kinetic data for the photoinduced electron transfer in hetero-tetrapyrrole arrays **7**–**9**.

Compound	Decay at 427 nm (τ [fs])	Increase at 620 nm (τ [fs])	Decay at 620 nm (τ [ps])
7	320	360	2.5
8	390	440	4.3
9	420	520	7.0

rates were even slower for tetrad **9** despite a similar porphyrin-to-double-decker separation to that of **8**. The results can be reasonably rationalized by considering the interaction between the two neighboring porphyrin chromophores in **9**. As revealed by a semiempirical (AM1) study,[26] the center-to-center distance between two porphyrin moieties connected at neighboring positions of a benzene ring through oxygen atoms is only approximately 1.1 nm (see Figure S4 in the Supporting Information), which is near enough for these two neighboring porphyrin chromophores to show electronic interactions.[27,28] As a consequence, a rapid and efficient energy transfer occurs between the two [Zn(TriBPP)] chromophores in **9**. It is noteworthy that the timescale of the energy-transfer process in the porphyrin dimer was found to be in the range of 10–100 ps,[29] which is much slower than that of the electron-transfer process from the porphyrin chromophore(s) to $[Eu(Pc)_2]$ in the present systems. It is therefore understandable that no significant change in the rate constant for the photoinduced electron transfer from the porphyrin chromophore(s) to $[Eu(Pc)_2]$ was detected for tetrad **9** as in the case of **8**. However, the recombination process of this compound was significantly retarded due to the interactions between the two [Zn(TriBPP)] moieties in tetrad **9** and the rate constant of the recombination process was reduced from $2.3\times10^{11}\,s^{-1}$ for **8** to $1.4\times10^{11}\,s^{-1}$ for **9**. In other words, the slowdown of the recombination process observed for tetrad **9** is actually attributed to the stabilization of the charge-separated state due to delocalization of the positive charge on the two interacting porphyrin chromophores of this tetrad. This is in line with the results reported for other similar supramolecular systems.[30]

Conclusion

Three novel phthalocyanine–porphyrin arrays containing a sandwich-type bis(phthalocyaninato)europium(III) core and one or two zinc(II) porphyrin unit(s) were designed and synthesized. Photophysical studies revealed that a rapid and efficient electron-transfer process from the porphyrin unit(s) to $[Eu(Pc)_2]$ occurs for all of these heteroarrays. The electron transfer, as well as the recombination process, was found to be dependent not only on the connecting position of the porphyrin chromophore onto the double-decker but also on the number of porphyrin moieties.

Experimental Section

General remarks: *n*-Pentanol was distilled from sodium. Dichloromethane for voltammetric studies was freshly distilled from CaH_2 under nitrogen. Column chromatography was carried out on silica gel (Merck, Kieselgel 60, 70–230 mesh) and biobead (BIORAD S-X1, 200–400 mesh) columns with the indicated eluents. All other reagents and solvents were used as received. The compounds $Eu(acac)_3\cdot nH_2O$,[31] [Eu(acac)(Pc)],[32] 5-(4-hydroxyphenyl)-10,15,20-tri(4-*tert*-butylphenyl)porphyrin (H_2TriBPPH),[33] and 5-(4-hydroxyphenyl)-10,15,20-tri(4-*tert*-butylphenyl)porphyrinato zinc [Zn(TriBPPH)],[13] were prepared according to the published procedures.

^{1}H NMR spectra were recorded on a Bruker DPX 300 spectrometer (300 MHz) in $CDCl_3$, [D6]DMSO, or $CDCl_3$/[D6]DMSO 1:1 with the addition of approximately 1 % hydrazine hydrate. Spectra were referenced internally by using the residual solvent resonance ($\delta = 7.26$ or 2.49 ppm for $CDCl_3$ and [D6]DMSO, respectively) relative to $SiMe_4$ (TMS). IR spectra were recorded as KBr pellets by using a BIORAD FTS-165 spectrometer with 2 cm^{-1} resolution. MALDI-TOF mass spectra were taken on a Bruker BIFLEX III ultrahigh resolution Fourier transform ion cyclotron resonance (FTICR) mass spectrometer with α-cyano-4-hydroxycinnamic acid as the matrix. Elemental analyses were performed by the Institute of Chemistry, Chinese Academy of Sciences, Beijing (China).

Electrochemical measurements were carried out with a BAS CV-50W voltammetric analyzer. The cell comprised inlets for a glassy-carbon-disk working electrode of 2.0 mm in diameter and a silver-wire counterelectrode. The reference electrode was Ag/Ag^+, which was connected to the solution by a Luggin capillary the tip of which was placed close to the working electrode. It was corrected for junction potentials by being referenced internally to the ferrocenium/ferrocene (Fe^+/Fe) couple ($E_{1/2}$ (Fe^+/Fe) = 501 mV versus the SCE). Typically, a 0.1 mol dm^{-3} solution of $[Bu_4N][ClO_4]$ in CH_2Cl_2 containing 0.5 mmol dm^{-3} of sample was purged with nitrogen for 10 min, then the voltammograms were recorded at ambient temperature. The scan rates were 20 and 10 mV s^{-1} for CV and DPV, respectively.

The absorption spectra were taken on a Hitachi 4100 UV/Vis/near-infrared (NIR) spectrometer, while the fluorescence spectra were recorded on a K2 system (ISS product) with excitation at 410 nm. Nanosecond transient absorption spectra were measured on a LP-920 pump–probe spectroscopic setup (Edinburgh). The excited source was the unfocused third harmonic (355 nm, 7 ns fwhm) output of a Nd:YAG laser (Continuum surelite II); the probe light source was a pulse-xenon lamp. The signals were detected by an Edinburgh LP900 analytical instrument and recorded on a Tektronix TDS 3012B oscilloscope and computer. Samples were bubbled with nitrogen for 15 min before measurements.

The femtosecond time-resolved spectrometer employed a regenerative amplifier Ti:sapphire femtosecond laser with 1 kHz repetition (Hurricane, Spectra Physics) as the primary beam source. The output energy of the laser was 750 mJ, with a pulse duration of 150 fs at 800 nm. The output beam was split into two; the part with an energy of 6 μJ pulse^{-1} was focused onto a 2.4 mm thick sapphire plate to generate a white light continuum as a probe source. Another beam was frequency doubled after passing a translation stage as a pump beam. A dual-beam configuration (probe and reference) was adopted for the detection. The probe and reference beams were collected by a pair of objective lenses coupled to a two-branched optical fiber. The spectra were recorded by a charge-coupled device spectrometer (Acton). The delay between the pump and the probe beams was realized by a computer-controlled translation stage. The polarization of the 400 nm pump beam was set to the magic angle (54.7°) with respect to the probe beam.[34,35]

{5-[4-(2,3-Dicyanophenyloxy)phenyl]-10,15,20-tris(4-*tert*-butylphenyl)porphyrinato}zinc(II) (2): A mixture of [5-(4-hydroxyphenyl)-10,15,20-tris(4-*tert*-butylphenyl)porphyrinato]zinc(II) (**1**; 431 mg, 0.5 mmol) and 3-nitrophthalonitrile (346 mg, 2.0 mmol) in dry DMF (10 mL) in the presence of K_2CO_3 (2.5 g, 16 mmol) was stirred at room temperature for 72 h. The resulting solution was then poured into cold water (100 mL) and stirred for another 30 min. The precipitate obtained by filtration was further purified by silica-gel column chromatography with $CHCl_3$ as the eluent (380 mg, 78 %): ^{1}H NMR (300 Hz, $CDCl_3$, 25 °C, TMS): $\delta = 1.57$–1.58 (d, 27 H; *t*Bu), 7.56–7.58 (d, 2 H; porphyrin (Por) phenyl-H), 7.79–7.81 (m, 7 H; Por phenyl-H + Por β-H), 8.08–8.11 (m, 6 H; Por phenyl-H), 8.17–8.18 (d, 1 H; Por β-H), 8.23–8.28 (m, 3 H; Por phenyl-H + Por β-H), 8.77–8.80 (m, 6 H; Por β-H + phthalonitrile H), 8.86–8.87 ppm (d, 2 H; phthalonitrile H); MS (GCT-MS): an isotopic cluster peaking at *m*/*z*: 988.3; calcd for [M]: 988.4 $^+$; elemental analysis: calcd (%) for $C_{64}H_{54}N_6OZn$: C 77.76, H 5.51, N 8.50; found: C 77.10, H 5.50, N 8.78.

{5-[4-(3,4-Dicyanophenyloxy)phenyl]-10,15,20-tris(4-*tert*-butylphenyl)porphyrinato}zinc(II) (3): A mixture of **1** (431 mg, 0.5 mmol), 4-nitrophthalonitrile (346 mg, 2.0 mmol), and K_2CO_3 (2.5 g, 16 mmol) in DMF (10 mL) was stirred at room temperature for 72 h. The resulting solution was then poured into cold water (100 mL) and stirred for another 30 min. The precipitate obtained by filtration was further purified by silica gel column chromatography with $CHCl_3$ as the eluent (416 mg, 85 %): ^{1}H NMR(300 Hz, $CDCl_3$, 25 °C, TMS): $\delta = 1.56$–1.57 (d, 27 H, *t*Bu), 7.59–7.61 (d, 2 H, Por phenyl-H), 7.77–7.81 (m, 7 H, Por phenyl-H + Por β-H), 7.95–8.02 (m, 2 H, Por β-H), 8.07–8.10 (m, 6 H, Por phenyl-H), 8.22–8.24 (m, 2 H, Por phenyl-H), 8.76–8.80 (m, 6 H, Por β-H + phthalonitrile H), 8.84–8.85 ppm (d, 2 H, phthalonitrile H); MS (GCT-MS): an isotopic cluster peaking at *m*/*z* 988.2; calcd for [M]$^+$: 988.4; elemental analysis: calcd (%) for $C_{64}H_{54}N_6OZn$: C 77.76, H 5.51, N 8.50; found: C 77.28, H 5.55, N 8.44.

4,5-Bis[(5,10,15-tris(4-*tert*-butylphenyl)-20-(4-phenyloxy)-porphyrinato)-zinc(II)]phthalonitrile (6): A mixture of 4,5-dichlorophthalonitrile (99 mg, 0.5 mmol), 5,10,15-tris(4-*tert*-butylphenyl)-20-(4-hydroxyphenyl)-porphyrin (**4**; 1.3 g, 1.5 mmol), and K_2CO_3 (7.5 g, 48 mmol) in DMF (20 mL) was stirred at 90 °C for 72 h. The resulting solution was cooled to room temperature and then poured into cold water (200 mL) and stirred for 30 min. The precipitate obtained by filtration was further purified by silica-gel column chromatography with $CHCl_3$ as the eluent followed by recrystallization from $CHCl_3$/MeOH to give the disubstituted product **5**. This compound (172 mg, 0.10 mmol) was then treated with Zn(acac)$_2$·2 H_2O (56 mg, 0.20 mmol) in DMF (10 mL) at 140 °C under a slow stream of nitrogen for 2 h. The solvent was then removed in vacuo and the residue was underwent chromatography on a silica-gel column with $CHCl_3$ as the eluent. The crude product was further purified by recrystallization from $CHCl_3$/MeOH to give the product as a pink powder (165 mg, 90 %): ^{1}H NMR (300 Hz, $CDCl_3$, 25 °C, TMS): $\delta = 1.10$ (s, 36 H; *t*Bu), 1.57 (s, 18 H; *t*Bu), 6.79–6.81 (d, 8 H; Por phenyl-H), 7.19–7.20 (d, 8 H; Por phenyl-H), 7.63–7.65 (d, 4 H; Por phenyl-H), 7.80–7.82 (d, 4 H; Por phenyl-H), 8.04–8.05 (d, 4 H; Por β-H), 8.09–8.11 (d, 4 H; Por phenyl-H), 8.21–8.23 (d, 4 H; Por phenyl-H), 8.54–8.55 (m, 4 H; Por β-H), 8.64–8.65 (m, 4 H; Por β-H), 8.65 (s, 2 H; phthalonitrile H), 8.73–8.74 ppm (d, 4 H; Por β-H); MS (GCT-MS): an isotopic cluster peaking at *m*/*z*: 1848.4; calcd for [M]$^+$: 1848.7; elemental analysis: calcd (%) for $C_{120}H_{104}N_{10}O_2Zn_2 \cdot 0.5\,CHCl_3$: C 75.83, H 5.52, N 7.34; found: C 75.17, H 5.63, N 7.40.

General procedure for the preparation of tetrapyrrole arrays 7–9: A mixture of [Eu(acac)(Pc)] (0.10 mmol), phthalonitrile (0.30 mmol), the porphyrinated phthalonitriles **2**, **3**, or **6** (0.10 mmol), and DBU (0.05 mL) in *n*-pentanol (4 mL) was heated to reflux at approximately 140 °C for 8 h under a slow stream of nitrogen. The resulting solution was cooled to room temperature, then the volatiles were removed under reduced pressure and the residue was purified by chromatography on a silica-gel column with $CHCl_3$ as the eluent to give a fraction containing both the desired heteroarrays and [Eu(Pc)$_2$] as a side product. The crude product was then loaded onto a bio-bead column with $CHCl_3$ as the eluent. The desired products were eluted as the first fraction. They were further purified by repeated chromatography on a bio-bead column followed by recrystallization from $CHCl_3$/MeOH.

Product **7**: Yield: 31 %; ^{1}H NMR (300 Hz, [D6]DMSO in the presence of approximately 1 % hydrazine hydrate, 25 °C, TMS): $\delta = 10.64$–11.18 (m, 15 H; Pc α-H), 8.98–9.20 (m, 15 H; Pc β-H), 8.88 (d, $J = 6.0$ Hz, 1 H; Pc β-H), 8.58–8.64 (m, 4 H; OC_6H_4), 7.67–8.17 (m, 16 H; Por β-H, *t*BuC_6H_4), 7.40 (s, 4 H; Por β-H), 1.77 (s, 18 H; *t*Bu), 1.48 ppm (s, 9 H; *t*Bu); MS (MALDI-TOF): an isotopic cluster peaking at *m*/*z*: 2037.8 [M]$^+$; elemental analysis calcd (%) for $C_{120}H_{82}EuN_{20}OZn$: C 70.74, H 4.06, N 13.75; found: C 70.39, H 4.20, N 13.63.

Product **8**: Yield: 40 %; ^{1}H NMR (300 Hz, $CDCl_3$/[D$_6$]DMSO 1:1 in the presence of approximately 1 % hydrazine hydrate, 25 °C, TMS): $\delta =$ 10.82–11.44 (m, 16 H; Pc α-H), 10.04 (d, $J = 4.5$ Hz, 2 H; OC_6H_4), 9.87 (d, $J = 4.5$ Hz, 2 H; OC_6H_4), 9.00–9.31 (m, 23 H; Pc β-H, Por β-H), 8.60–8.68 (m, 4 H; *t*BuC_6H_4), 8.27–8.31 (m, 6 H; *t*BuC_6H_4), 7.91 (d, $J = 9.0$ Hz, 2 H; *t*BuC_6H_4), 2.07 (s, 18 H; *t*Bu), 1.71 ppm (s, 9 H; *t*Bu); MS (MALDI-TOF): an isotopic cluster peaking at *m*/*z*: 2038.8 [M+H]$^+$; elemental analysis calcd (%) for $C_{120}H_{82}EuN_{20}OZn$: C 70.74, H 4.06, N 13.75; found: C 70.10, H 4.16, N 13.44.

Product **9**: Yield: 33 %; ^{1}H NMR (300 Hz, $CDCl_3$/[D6]DMSO 1:1 in the presence of approximately 1 % hydrazine hydrate, 25 °C, TMS): $\delta =$ 10.80–11.26 (m, 16 H; Pc α-H), 9.88 (d, $J = 4.5$ Hz, 4 H; OC_6H_4), 9.41 (d, $J = 4.5$ Hz, 4 H; OC_6H_4), 8.91–9.29 (m, 30 H; Pc β-H, Por β-H), 8.20–8.28 (m, 12 H; *t*BuC_6H_4), 7.82–7.90 (m, 12 H; *t*BuC_6H_4), 1.78 (s, 36 H; *t*Bu), 1.61 ppm (s, 18 H; *t*Bu); MS (MALDI-TOF): an isotopic cluster peaking at *m*/*z*: 2898.0 [M+H]$^+$; elemental analysis calcd (%) for $C_{176}H_{132}EuN_{24}O_2Zn_2$: C 72.95, H 4.59, N 11.60; found: C 72.31, H 4.75, N 11.47.

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