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Lanthanide(III) Bis(phthalocyaninato)–[60]Fullerene Dyads: Synthesis, Characterization, and Photophysical Properties

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Abstract: A novel series of double-decker lanthanide(III) bis(phthalocyaninato)–C_{60} dyads $[Ln^{III}(Pc)(Pc')]$–C_{60} (M = Sm, Eu, Lu; Pc = phthalocyanine) (**1a**–**c**) have been synthesized from unsymmetrically functionalized heteroleptic sandwich complexes $[Ln^{III}(Pc)(Pc')]$ (Ln = Sm, Eu, Lu) **3a**–**c** and fulleropyrrolidine carboxylic acid **2**. The sandwich complexes **3a**–**c** were obtained by means of a stepwise procedure from unsymmetrically substituted free-base phthalocyanine **5**, which was first transformed into the monophthalocyaninato intermediate $[Ln^{III}(acac)(Pc)]$ and further reacted with 1,2-dicyanobenzene in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). ^{1}H NMR spectra of the bis(phthalocyaninato) complexes **3a**–**c** and dyads **1a**–**c** were obtained by adding hydrazine hydrate to solutions of the complexes in $[D_7]$DMF, a treatment that converts the free radical double-deckers into the protonated species, that is, $[Ln^{III}(Pc)(Pc')H]$ and $[Ln^{III}(Pc)(Pc')H]$–C_{60}. The electronic absorption spectra of **3a**–**c** and **1a**–**c** in THF exhibit typical transitions of free-radical sandwich complexes. In the case of dyads **1a**–**c**, the spectra display the absorption bands of both constituents, but no evidence of ground-state interactions could be appreciated. When the UV/Vis spectra of **3a**–**c** and **1a**–**c** were recorded in DMF, typical features of the reduced forms were observed. Cyclic voltammetry studies for **3a**–**c** and **1a**–**c** were performed in THF. The electrochemical behavior of dyads **1a**–**c** is almost the exact sum of the behavior of the components, namely the double-decker $[Ln^{III}(Pc)(Pc')]$ and the C_{60} fullerene, thus confirming the lack of ground-state interactions between the electroactive units. Photophysical studies on dyads **1a**–**c** indicate that only after irradiation at 387 nm, which excites both C_{60} and $[Ln^{III}(Pc)(Pc')]$ components, a photoinduced electron transfer from the $[Ln^{III}(Pc)(Pc')]$ to C_{60} occurs.

Keywords: fullerenes • lanthanides • phthalocyanines • sandwich complexes

Introduction

Phthalocyanines (Pcs)[1] are an important class of chromophores that have fascinated scientists for many years due to their applicability in different fields, such as nonlinear optics,[2] organic solar cells,[3,4] and field-effect transistors.[5] This range of applications arises from the ease of tuning specific properties through the introduction of substituents at the aromatic ring and through the incorporation of up to 70 different metallic or metalloid elements into the central cavity of the macrocyclic ligand (Pc^{2-}). A large number of metal ions, the ionic radii of which exceed what has been called the "coordination space" of the dinegative quadridentate phthalocyaninato ligand, cannot enter the central cavity of the Pc ring.[6] These metal ions (Ln^{3+}, Sc^{3+}, Y^{3+}, Ce^{4+}, etc.) prefer to have coordination numbers larger than six, eight being the most common in lanthanide(III) phthalocyaninato derivatives, thus displaying a sandwich-like structure. Lanthanide(III) bis(phthalocyaninato) complexes pos-

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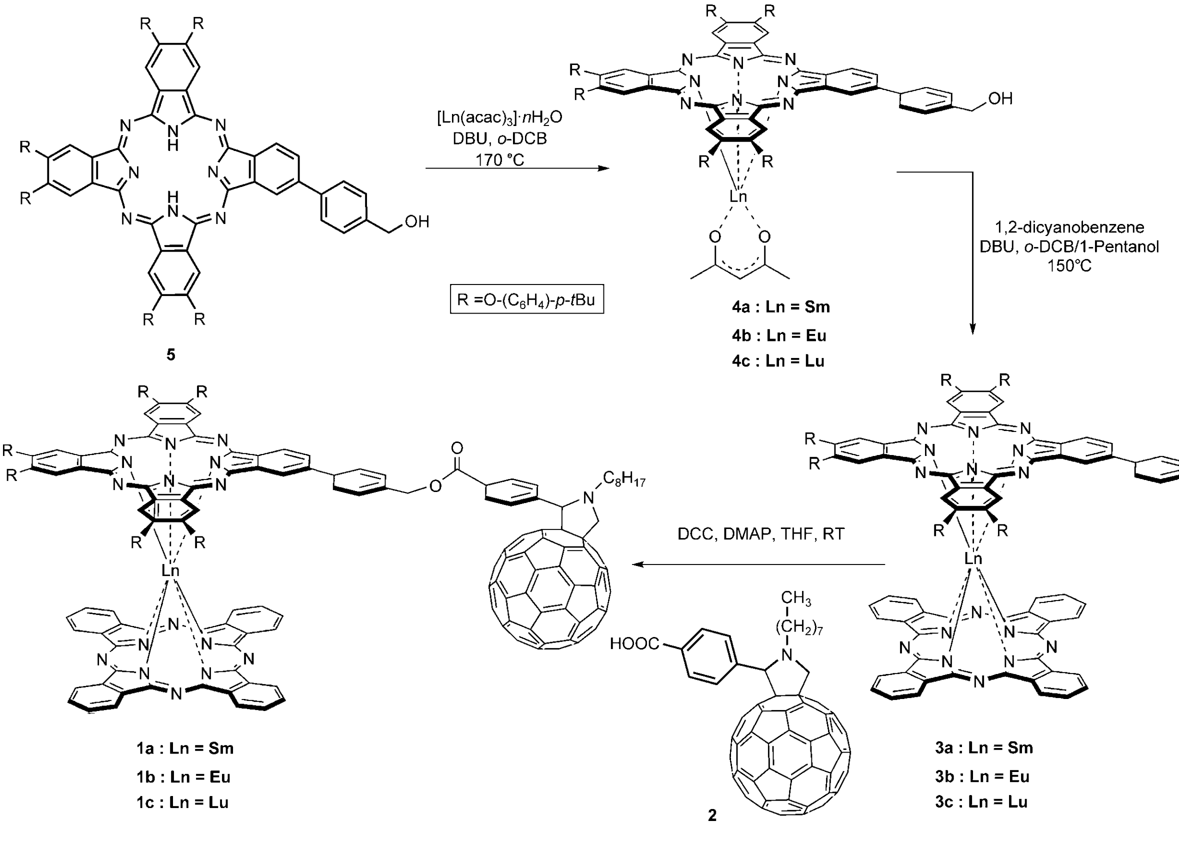
sess intriguing and unique electronic and optical properties that make them useful in materials science, because of their possible applications in molecular electronics, molecular information storage, and nonlinear optics.[7] Rare-earth-metal bisphthalocyanines are well explored electrochromic materials, which are readily oxidized and reduced and exhibit several colors.[8] The most familiar states are the "green" form, a free-radical species in which one of the Pc rings possesses 17 electrons, and the "blue" form, obtained by one-electron reduction. The blue form requires the presence of an "extra hydrogen" to achieve charge neutrality, but its location is unclear.[9]

The chemistry of sandwich-type complexes comprising two identically functionalized Pc rings (homoleptic complexes) has been studied for several decades.[10] In recent years, heteroleptic rare-earth bis(phthalocyanines) composed of two differently substituted Pc rings have been also investigated, as well as other heteroleptic sandwich-type complexes with different combination of tetrapyrrolic units in a double- or triple-decker arrangement.[11,12]

However, just a few examples of bis(phthalocyaninato) complexes holding one unsymmetrically functionalized Pc ring can be found in the literature.[13] The incorporation of Pc cores bearing solubilizing moieties at three isoindole units and one reactive group at the remaining position, would allow the attachment of this type of complexes to other chromophore or electronic subunit in order to study energy and electron transfer processes.[14]

Due to its extensive π-electron conjugation C_{60} has been widely investigated for potential applications in different fields.[15] C_{60} and its derivatives can reversibly accept up to six electrons, because of their triply degenerate low-lying LUMOs.[16] These features render C_{60} an ideal electron-acceptor molecule in donor–acceptor (D–A) systems designed to mimic the photosynthetic reaction center.[17] In this regard, we have previously described the preparation of strongly coupled Pc–C_{60} dyads in which long-lived photoinduced charge-separated states are formed.[18] In these systems, phthalocyanines behave as the electron-donor partner.

Lanthanide(III) double-deckers show lower oxidation potentials than mononuclear Pcs and, for this reason, they are interesting candidates to be utilized as donor components in D–A dyads or as active components in solar cells.[14,19] The current work is expected to make a significant contribution to this field of research. In this context, we describe in detail the synthesis, and the electrochemical and photophysical characterization of a set of three $[Ln^{III}(Pc)(Pc')]$–C_{60} complexes (**1a–c**; Scheme 1) bearing different lanthanide ions. To the best of our knowledge, these compounds represent the first example of double-decker lanthanide(III) bis(phthalocyaninato)–C_{60} dyads.



Scheme 1. Synthesis of [Ln(Pc)(Pc′)] double-deckers **3a–c** and the corresponding [Ln(Pc)(Pc′)]–C_{60} dyads **1a–c**.

Results and Discussion

Synthesis and spectroscopic characterization: The classical method for the preparation of homoleptic sandwich compounds involves the self-condensation of phthalonitriles in the presence of metal salts.[20] Regarding heteroleptic rare-earth bis(phthalocyaninato) compounds, two main synthetic pathways have been reported thus far for the preparation of this kind of complexes. The first method involves the reaction of a rare-earth salt with two different lithium or metal-free phthalocyanines, $H_2/Li_2(Pc)$ and $H_2/Li_2(Pc')$.[21] However, as expected, this reaction also produced the corresponding homoleptic sandwich compounds, which can be separated only by repeated chromatographic procedures. To overcome that drawback, an improved method, which involves the formation of intermediate mononuclear lanthanide(III) complexes ($[Ln^{III}(X)(Pc)]$, X = acetyl, acetylacetonate ligand) followed by cyclic tetramerization of substituted phthalonitriles over the preformed monophthalocyaninate, has been reported in recent years.[22]

In the present work, we have employed a similar stepwise procedure for the preparation of heteroleptic sandwich complexes **3a–c** (Scheme 1), which are composed of one unsymmetrically substituted Pc (holding six solubilizing *p-tert*-butylphenoxy moieties and one reactive hydroxymethylphenyl one) and a "nacked" Pc ligand, using the corresponding lanthanide(III) acetylacetonate ($[Ln^{III}(acac)_3]\cdot n\,H_2O$, Ln = Sm, Eu, Lu), phthalonitrile, and unsymmetrically substituted metal-free phthalocyanine (H_2Pc; **5**)[23] as starting materials. In a first step, $[Ln^{III}(acac)(Pc)]$ (**4a–c**) were generated through reaction of $[Ln^{III}(acac)_3]\cdot n\,H_2O$ and **5** at about 170 °C in *o*-dichlorobenzene (*o*-DCB). The formation of the mononuclear complexes **4a–c** was monitored by UV/Vis experiments, in which one can appreciate a decrease in the intensity of the two bands of **5**, centered at 706 and 672 nm, and the growing of a new band centered at approximately 685 nm. All three lanthanide(III) complexes were fully formed in 1.5 h. After removal of the solvents, the mononuclear intermediates were reacted, without further purification, with dicyanobenzene in the presence of DBU in *o*-DCB/1-pentanol at 160 °C, yielding the corresponding heteroleptic double-deckers **3a–c**. These lanthanide(III) bis(phthalocyaninato) complexes are obtained as a mixture of the free-radical $[Ln^{III}(Pc)(Pc')]$ (green forms) and the corresponding reduced protonated complexes $[Ln^{III}(Pc)(Pc')H]$. In each case, purification of the mixture was performed by repeated silica gel column chromatography with chloroform as eluent. Oxidation of the blue forms was observed when eluting along the column. As a result, the corresponding radical species $[Ln^{III}(Pc)(Pc')]$ (**3a–c**) were isolated in about 20 % yield. $[Ln^{III}(Pc)(Pc')]$–C_{60} dyads (**1a–c**) were prepared by esterification reaction between the corresponding $[Ln^{III}(Pc)(Pc')]$ (**3a–c**) and 4-(1′-octyl-3′,4′-fulleropyrrolidin-2′-yl)benzoic acid (**2**)[24] in the presence of DMAP and DCC. A partial reduction of the complexes was observed because of the presence of DMAP, leading to a mixture of the radical dyads $[Ln^{III}(Pc)(Pc')]$–C_{60} (green forms) and the corresponding reduced protonated $[Ln^{III}(Pc)(Pc')H]$–C_{60} (blue forms). Purification of the dyads was carried out by exclusion size chromatography and repeated silica gel column chromatography, which ended in the oxidation of the blue forms to the green ones. In this way, radical dyads $[Ln^{III}(Pc)(Pc')]$–C_{60} (**1a–c**) were obtained in approximately 50 % yield.

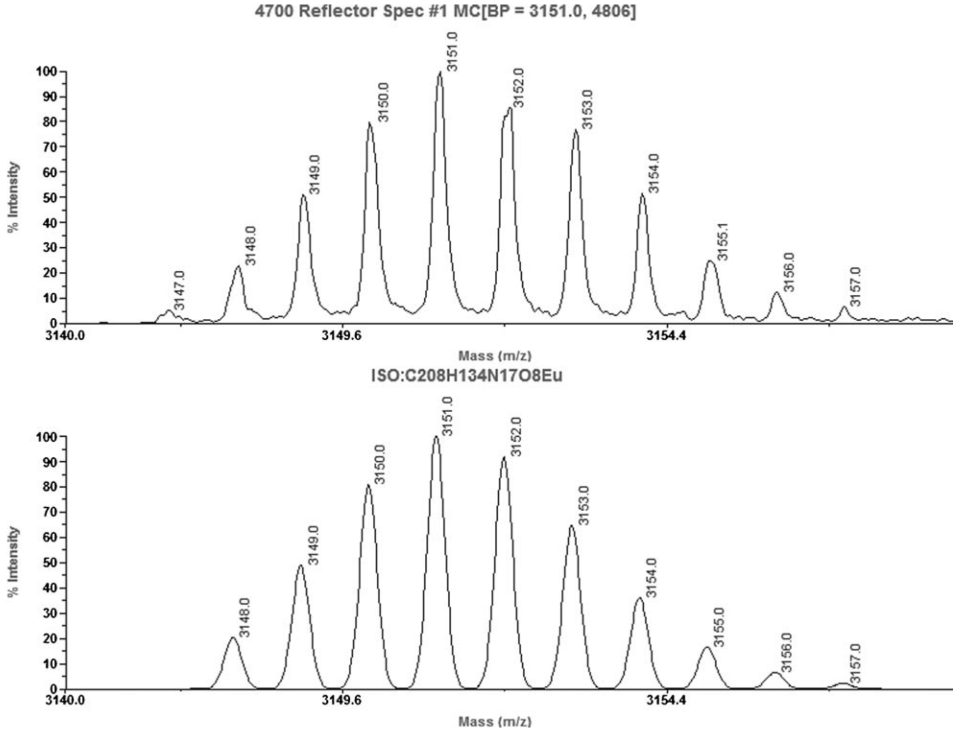


Figure 1. Top: partial MALDI-TOF mass spectrum of **1b**, showing the isotopic distribution of the molecular ion. Bottom: corresponding simulated pattern.

Compounds **3a–c** and **1a–c** gave satisfactory elemental analysis data. Their sandwich nature was further unambiguously confirmed by various spectroscopic methods. MALDI-TOF spectra of all these double-deckers showed an isotopic pattern in good agreement with the simulated spectrum. This is exemplified in Figure 1, which depicts the theoretical and experimental spectrum of dyad **1b**. The IR spectra of all the bis(phthalocyaninato) complexes (**3a–c**) and their corresponding dyads (**1a–c**) showed an intense band at

1318–1325 cm^{-1} (Figure S5 and S8 in the Supporting Information), which shifts to higher wavenumbers along with the lanthanide contraction, and is a marker band for the Pc π radical,[25] as it is also manifested in the UV/Vis spectra (see below).

^{1}H NMR spectra: Because of the presence of the unpaired electron, NMR data for all the single-hole lanthanide(III) bis(phthalocyaninato) complexes are difficult to obtain. However, upon addition of hydrazine hydrate as reducing agent, well-resolved ^{1}H NMR spectra (Figure S1 and S6 in the Supporting Information) could be recorded for the reduced blue forms of all the heteroleptic double-deckers **1a–c** and **3a–c** (i.e., [Ln^{III}(Pc^{2-})(Pc$'^{2-}$)H] and [Ln^{III}(Pc^{2-})(Pc$'^{2-}$)H]–C$_{60}$), as both macrocyclic ligands become diamagnetic anions. The use of [D$_7$]DMF as deuterated solvent was necessary to completely reduce the radical forms of **3a–c** and **1a–c**, as well as the addition of one drop of CCl$_4$ to fully dissolve all the complexes. Figure 2 shows the ^{1}H NMR spectra of the reduced forms of **3b** and **1b** in the region from 12 to 2 ppm. As a general rule, the α protons of the unsubstituted Pc ring resonate at lower field followed by the α′ protons of the substituted Pc ring. The β and β′ protons appear at higher field. In particular, the europium(III) derivatives [Eu^{III}(Pc)(Pc′)H] and [Eu^{III}(Pc)(Pc′)H]–C$_{60}$ show down-field shifts for all the resonances with respect to the Sm^{III} and Lu^{III} derivatives. The presence of C$_{60}$ in all reduced forms (i.e., [Ln^{III}(Pc)(Pc′)H]–C$_{60}$) of complexes **1a–c** induces broadening of the signals, but still the typical pattern of resonances can be distinguised.

Ground-state electronic absorption spectra: Electronic absorption spectra of compounds **1a–c** and **3a–c** were recorded in CHCl$_3$ (Figure 3 and S2 in the Supporting Information). The spectra of the neutral double-deckers complexes [Ln^{III}(Pc)(Pc′)] (**3a–c**) and their dyads [Ln^{III}(Pc)(Pc′)]–C$_{60}$ (**1a–c**) exhibit typical features of single-hole bis(phthalocyaninates).[7] All the absorption spectra show a typical Soret band at 320-326 nm with a shoulder at the lower-energy side, involving a couple of electronic transitions dealing with the third occupied HOMO and the first LUMO. It is worth noting that similar splitting of the Soret band had been previously observed for other homo- and heteroleptic bis(phthalocyaninato) rare-earth complexes.[8e,22b,26] The Q bands for these compounds appear in the 670–680 nm range (with two vibrational shoulders at 588–590 and 603–615 nm) resulting from the transitions from the first semi-occupied molecular orbital (SOMO) to the second LUMO and from the second fully occupied HOMO to the first LUMO.[27] In addition, the two weak π-radical bands at about 460–490 nm and 913–922 nm can be attributed to the electronic transitions involving the

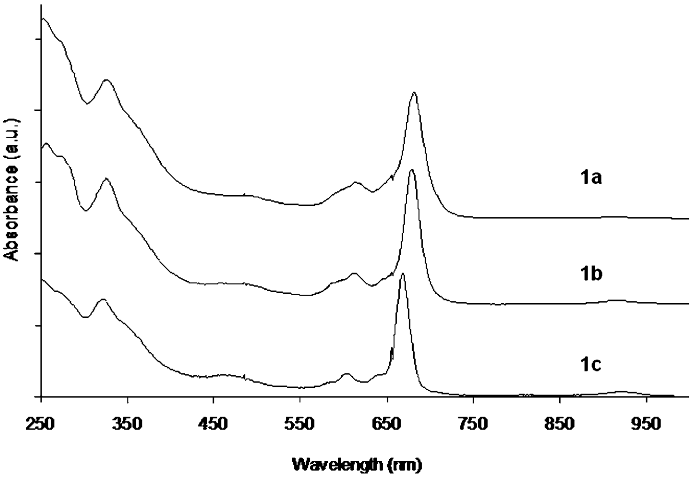


Figure 3. Electronic absorption spectra of **1a–c** complexes in CHCl$_3$.

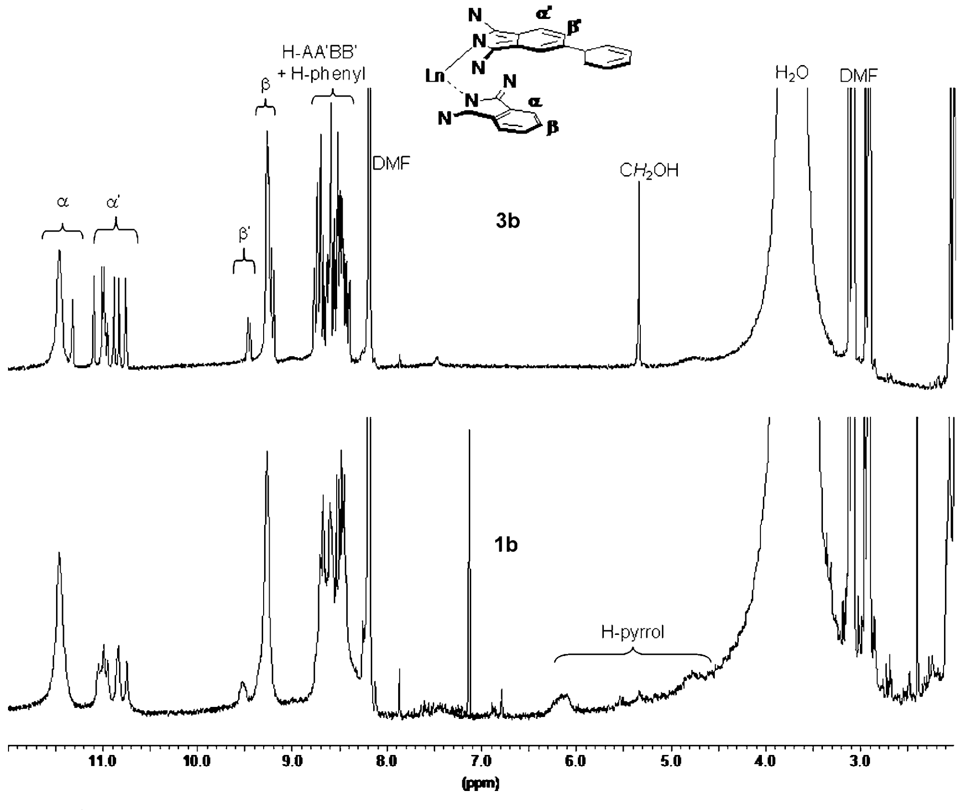
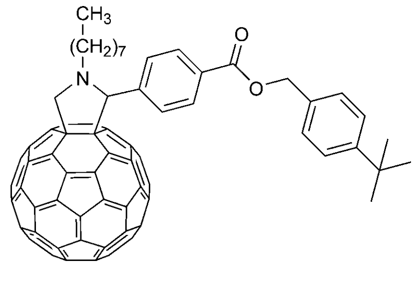


Figure 2. ^{1}H NMR spectra of [Eu^{III}(Pc)(Pc′)H] (reduced form of **3b**) and [Eu^{III}(Pc)(Pc′)H]–C$_{60}$ (reduced form of **1b**) in [D$_7$]DMF/CCl$_4$/N$_2$H$_4$.

SOMO. With exception of the π-radical band at abour 915 nm, the absorption wavelengths of all the other bands experiment hypsochromic shifts when the ionic radii of the lanthanide cations decrease (from Sm to Lu), because the interaction between the two rings becomes stronger. The spectra of dyads **1a–c** is a linear superimposition of the absorption of the individual components; that is, the lanthanide(III) bis(phthalocyaninato) unit and the fullerene one, thus indicating the lack of ground-state interactions between the subunits.

When the UV/Vis spectra of **3a–c** and **1a–c** were recorded in DMF, a progressive formation of the anionic blue forms was observed (Figure S3 in the Supporting Information). The absorption spectra of the protonated species [Ln^{III}(Pc)(Pc′)H] (Figure S4 and S7 in the Supporting Information) resemble those of double-deckers containing two dianionic ligands, such as [Ce^{IV}(Pc)(Pc′)],[28] [M^{IV}(Pc)(Pc′)] (M = Zr, Hf, Th, U),[29] and Li[M^{III}(Pc)(Pc′)] (M = Eu, Gd).[30] The spectra show medium-to-high intense Soret bands at 340 nm, and split Q bands in the 620–700 nm region; this splitting is more prominent for the heavier lanthanides (from Sm to Lu). In the case of the protonated [Ln^{III}(Pc)(Pc′)H]–C_{60} dyads, the absorption spectra are also a superimposition of the features of both constituents.

Ground-state electrochemistry: The solution electrochemistry of dyads **1a–c** was studied using cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV). The results obtained for **1a–c** were compared with those of the model lanthanide(III) bis(phthalocyaninato) complexes **3a–c** and the fulleropyrrolidine compound **6**. For comparative purposes, **6** was synthesized through an esterification reaction between **2** and 4-*tert*-butylphenylmethanol (see Experimental Section). The CV results are presented in Figure 4 and the potential data collected in Table 1.



6

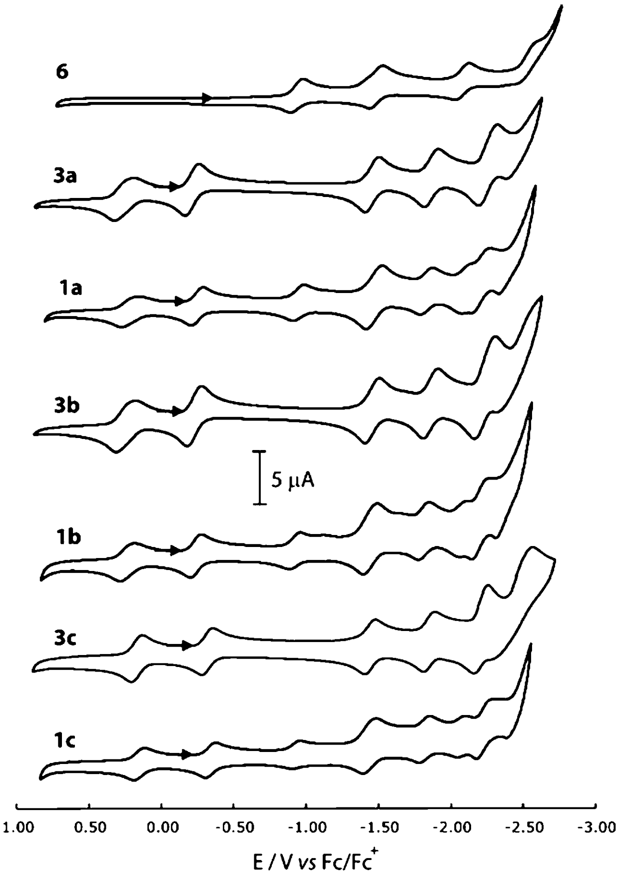


Figure 4. CVs of bis(phthalocyaninato) complexes **3a–c**, dyads **1a–c**, and reference compound **6** in THF at room temperature.

Within the electrochemical window of THF, all the double-decker compounds **3a–c** undergo one quasi-reversible one-electron oxidation and up to four quasi-reversible one-electron reductions (Figure 5 and Figure S11 in the Supporting Information). All these redox processes can be attributed to the successive removal or addition of electrons from/or to the ligand-based orbitals, as the trivalent lanthanide(III) center cannot be oxidized or reduced under these conditions. As in many other series of double-deckers, the redox potentials of **3a–c** depend on the ionic radius of the metal center.[8g,11,12c] As shown in Table 1, the half-wave potentials of the oxidation and the first reduction processes, both of which involve the SOMO orbital, shift slightly in the negative direction as the metal center decreases.

The potentials for the remaining three reduction processes are insensitive to the ionic size of the lanthanide(III) center, suggesting that the energy level of the LUMO does not change significantly with the metal center. According to the orbital scheme depicted in Figure 5, $\Delta E^{0}_{1/2}$ (potential difference between the first oxidation and the first reduction process), represents the energy of putting a second electron in the SOMO of the neutral double-decker radical **3a–c** or removing one of the two electrons from the HOMO of the corresponding reduced double-decker species [Ln^{III}(Pc)(Pc′)]$^-$. For all the compounds $\Delta E^{0}_{1/2}$ spans a very narrow range (i.e., 0.47–0.49 V), which correlates well with previous reported results for bis(phthalocyaninato) complexes.[8g,12c]

Furthermore, the potential difference between the first and second reduction processes for compounds **3a–c** corresponds to the potential difference between the first oxidation and the first reduction of [Ln^{III}(Pc)(Pc′)]$^-$, $\Delta E^{0\prime}_{1/2}$ (Table 1). The values range from 1.12 V (**3c**) to 1.23 V (**3b**) and 1.25 V (**3a**), diminishing gradually with the decrease of

Table 1. Electrochemical data [mV vs. Fc/Fc$^+$] for bis(phthalocyaninato) complexes **3a–c**, dyads **1a–c**, and reference compound **6** in THF.

	$E^1_{1/2,ox}$ [a]	$E^1_{1/2,red}$ [a]	$E^2_{1/2,red}$ [b]	$E^3_{1/2,red}$ [a,b]	$E^4_{1/2,red}$ [a]	$E^5_{1/2,red}$ [b]	$E^6_{1/2,red}$ [a]	$\Delta E^0_{1/2}$ [c]	$\Delta E^{0\prime}_{1/2}$ [d]
6			−1008	−1574		−2187			
3a	+206	−261		−1506	−1914		−2371	0.47	1.25
1a	+184	−296	−1020	−1558	−1932	−2306	−2388	0.48	0.72
3b	+192	−278		−1506	−1910		−2352	0.47	1.23
1b	+203	−288	−955	−1529	−1914	−2226	−2390	0.49	0.67
3c	+114	−371		−1493	−1901		−2261	0.49	1.12
1c	+114	−395	−1007	−1531	−1921	−2211	−2410	0.51	0.61

[a] Bis(phthalocyaninato)-complex-based redox process. [b] C_{60}-based reduction. [c] $\Delta E^0_{1/2}$ in V, is the energy required to put a second electron in the SOMO of the neutral double-decker radical [Ln^{III}(Pc)(Pc′)] or to remove one electron of the two from the HOMO of the reduced double-decker species [Ln^{III}(Pc)(Pc′)]$^-$: $E^1_{1/2,ox}-E^1_{1/2,red}$. [d] $\Delta E^{0\prime}_{1/2}$ in V, is the potential difference between the first reduction and the second reduction processes, that is, the HOMO–LUMO gap of the reduced double-decker species [Ln^{III}(Pc)(Pc′)]$^-$ or [Ln^{III}(Pc)(Pc′)]$^-$–C_{60}: $\Delta E^{0\prime}_{1/2}=E^1_{1/2,red}-E^2_{1/2,red}$.

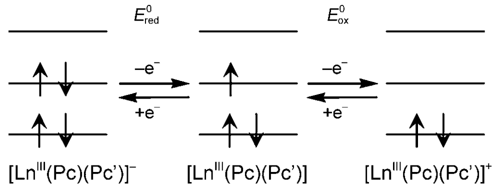


Figure 5. Frontier orbitals and first one-electron redox processes of [Ln^{III}(Pc)(Pc′)] compounds.

the lanthanide(III) ion radius, which clearly shows a size effect and indicates the enhanced π–π interactions in the double-deckers with smaller lanthanides compared with that connected by larger lanthanides. As the first reduction step and second reduction step of **3a–c** (or the first oxidation and first reduction of the corresponding reduced forms [Ln^{III}(Pc)(Pc′)]$^-$), involve the HOMOs and the LUMOs, respectively, of the molecules, the energy difference between these two redox processes corresponds to their electrochemical molecular band gap.

The cyclic voltammograms of dyads **1a–c** are similar to those of **3a–c**. All dyads are electrochemically active in both anodic and cathodic directions and the electrochemistry of the three species is almost the exact sum of the behavior of the independent components: the double-decker [Ln^{III}(Pc)(Pc′)] and the C_{60} portions. Thus, in the anodic direction, **1a–c** show one double-decker-based one-electron quasi-reversible oxidation wave. In the cathodic direction, between 0 and −2.5 V, dyads **1a–c** show six quasi-reversible reduction waves that can be easily assigned either to the C_{60} or the double-decker [Ln^{III}(Pc)(Pc′)] moieties when compared to those of **3a–c** and **6**. The first reduction wave corresponds in all dyads to the first reduction of the double-decker, and, as in reference systems **3a–c**, the potentials shift to negative values when decreasing the ionic radii of the metal center. The second reduction process in **1a–c** corresponds in all cases to the first reduction of the C_{60} core. The obtained reduction potentials (between −955 and −1020 mV) are typical of fullerene mono-adducts.[18] The third reduction wave is a two-electron process, which involves the second reduction of the C_{60} core and the second reduction of the double-decker [Ln^{III}(Pc)(Pc′)] moiety. The fourth and sixth reduction waves correspond again to reductions on the double-decker moiety, whereas the fith reduction is C_{60}-based.

The potential difference between the first oxidation process and the first reduction process for dyads **1a–c** ($\Delta E^0_{1/2}$) is almost independent of the ionic radius of the metal center, although the values are slightly larger than those of model systems **3a–c**. It is also worth mentioning that the potential difference between the first reduction of the [Ln^{III}(Pc)(Pc′)] moiety and the first reduction of the C_{60} addend corresponds to the electrochemical molecular band gap, which ranges from 0.61 to 0.72 V across the series, gradually diminishing with the decrease of lanthanide(III) radius.

Photophysics: The photophysical section focuses exclusively on the excited state interactions between the two electroactive moieties in **1a–c** (i.e., [Ln^{III}(Pc)(Pc′)] and C_{60}) involving the free radical species of the lanthanide(III) double-decker complexes, but not the corresponding reduced forms.

Considering the dominant absorptions of the [Ln^{III}(Pc)(Pc′)] derivatives **3a–c** all throughout the visible region, we focused on their fluorescence features upon 330, 335, and 675 nm excitation. A fluorescence pattern evolves that is a mirror image to the ground-state absorptions, with maxima in the visible at around 690 nm that resembles that of structurally simpler metallated phthalocyanines (i.e., Zn^{II}Pc, etc.). Figure 6 illustrates the sharp fluorescence maxima that were recorded for **3c** and **3a** at 695 nm, while in the case of **3b** the maxima are seen to split into a set of two, at 687 and 705 nm. The overall trend resembles, nevertheless, that seen in the absorption characteristics. Despite the apparent similarity between mononuclear metallated phthalocyanines (i.e, Zn^{II}Pc), on one hand, and **3a–c**, on the other hand, the overall quantum yields differ largely (0.3 versus 0.004). In reference to the long wavelength absorption (i.e., 900–950 nm), no emission was discernable. When turning to the corresponding electron donor–acceptor [Ln^{III}(Pc)(Pc′)]–C_{60} conjugates **1a–c**, it is remarkable that the Pc-centered fluorescence reveals negligible impacts. At the very best, the fluorescence of the [Lu^{III}(Pc)(Pc′)] moiety in **1c** seems to be affected, relative to what is seen in **3c**. Moreover, it is interesting to note the lack of the characteristic C_{60}-centered fluorescence features, which could have originated from direct excitation of the C_{60} moiety (i.e., 330 and 335 nm ex-

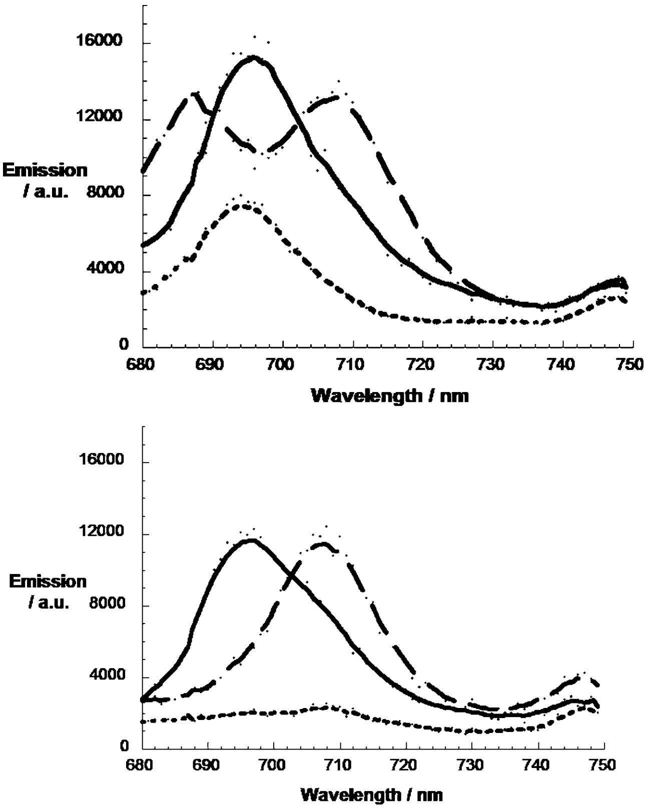


Figure 6. Steady-state fluorescence spectra of double-deckers—upper part: **3a** (solid line), **3b** (dashed line), **3c** (dotted line)—and the corresponding dyads—lower part: **1a** (solid line), **1b** (dashed line), **1c** (dotted line) in toluene at 335 nm excitation.

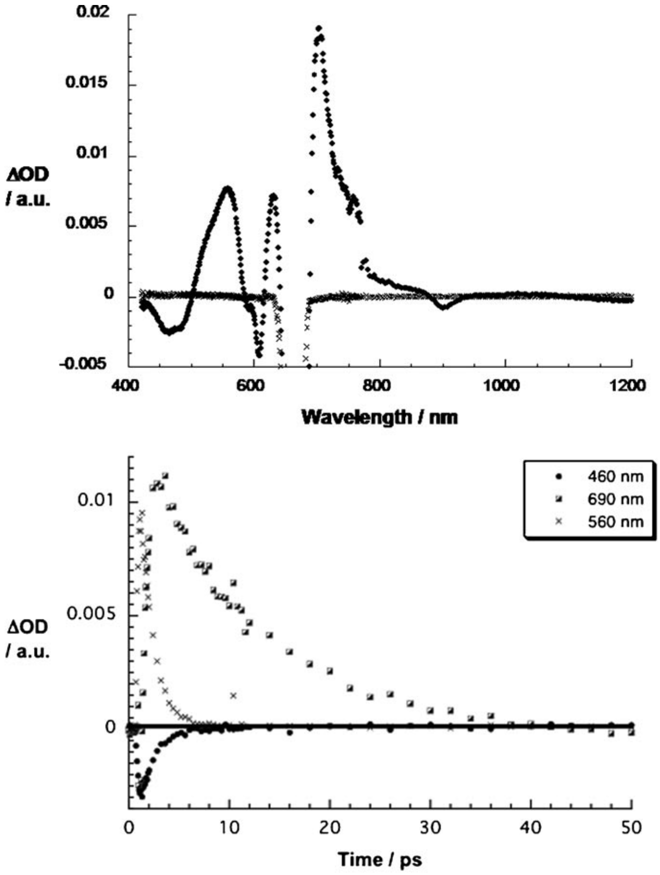


Figure 7. Upper part: differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (665 nm) of **3a** in nitrogen-saturated toluene with time delays of 1 ps (filled circles) and 50 ps (crosses) at room temperature. Lower part: time-absorption profiles of the spectra shown above at 460, 560, and 690 nm, monitoring the excited-state formation and deactivation.

citation) or through energy transfer from the photoexcited [Ln^{III}(Pc)(Pc′)] center (i.e., 675 nm excitation). Time-resolved measurements of **3a–c** and donor–acceptor dyads **1a–c** failed to provide any meaningful insight into the radiative deactivation of the photoexcited lanthanide(III) double-deckers and their corresponding C_{60} conjugates. A possible rationale implies a rapid deactivation - less than the time resolution of our experimental set up of 200 ps, which is in line with the low fluorescence quantum yields.

Next, we turned to femtosecond transient absorption measurements to conduct excitation experiments at 387 or 665 nm, which photoexcite the [Ln^{III}(Pc)(Pc′)] and C_{60} centers simultaneously (i.e., 387 nm) or the [Ln^{III}(Pc)(Pc′)] exclusively (i.e., 665 nm). First, we performed the experiments on the sandwich complexes **3a–c**. In accordance with the ground-state features, transient minima, in the form of bleach, occur at 460, 600, 675, and 900 nm, while transient maxima appear at 555, 630, 705, and 955 nm (see Figure 7) for compounds **3a**,**b**. In the case of **3c**, a slight difference is discernable, with minima and maxima that were found at 460, 573, 597 and 620, 698, 915, 960 nm, respectively. Taking the open-shell character of **3a–c** into consideration, their doublet ground state is instantaneously transformed (< 0.5 ps) into the doublet excited state. The doublet excited state of these lanthanide(III) double-deckers is, however, intrinsically unstable and gives intersystem crossing with a lifetime of 3.5 ps to the corresponding quartet excited state. Spectroscopic features of the latter excited state include, in all cases, maxima that are shifted relative to those of the doublet excited state, namely at 520, 620, 695 and 1020 nm. Figure 7 documents that the quartet excited state features are also short lived, with an underlying lifetime of 16 ps. The photoreactivity of **3a–c** is somewhat changed when using 387 nm excitation—compare Figures 7 and 8. In particular, new transients with maxima at 550 and 840, and minima at 705 nm develop simultaneously with the decay of the quartet excited state in all cases. Notable is an overall reminiscence with features that are linked to the one-electron oxidized forms of mononuclear H_2Pc, Zn^{II}Pc, Ru^{II}Pc, etc. In other words, excitation into the Soret-band region of complexes **3a–c** seems to trigger a photochemical reaction like that seen for Mg^{II}Pc.[31]

In the corresponding [Ln^{III}(Pc)(Pc′)]–C_{60} dyads **1a–c**, excitation at 665 nm leads to the same sequence of rapid excited state deactivation, that is, doublet-to-quartet intersystem crossing (i.e., 3.5 ps) and ground state recovery (i.e., 16 ps), that is seen with sandwich complexes **3a–c**. An example

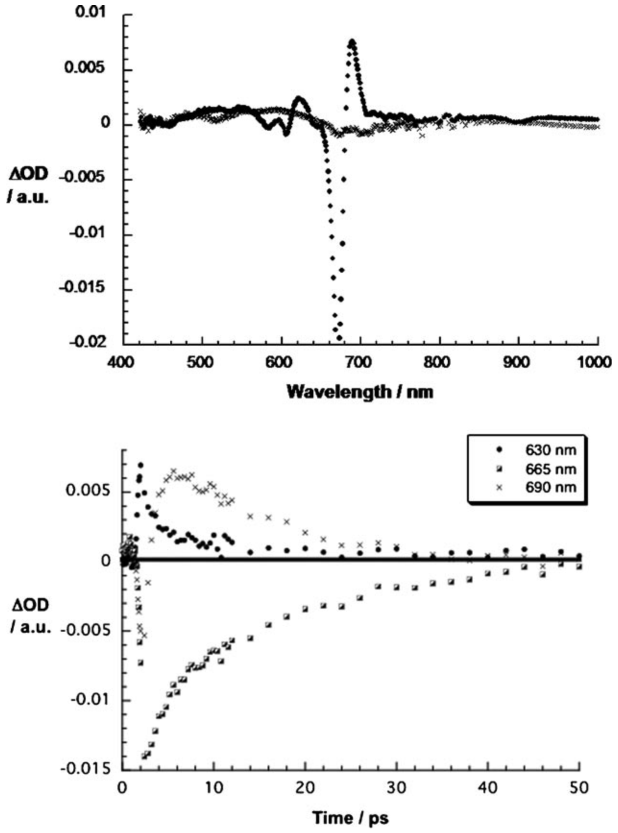


Figure 8. Upper part: differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (387 nm) of **3a** in nitrogen-saturated toluene with time delays of 1 ps (filled circles) and 50 ps (crosses) at room temperature. Lower part: time-absorption profiles of the spectra shown above at 630, 665, and 690 nm monitoring the excited-state formation and deactivation.

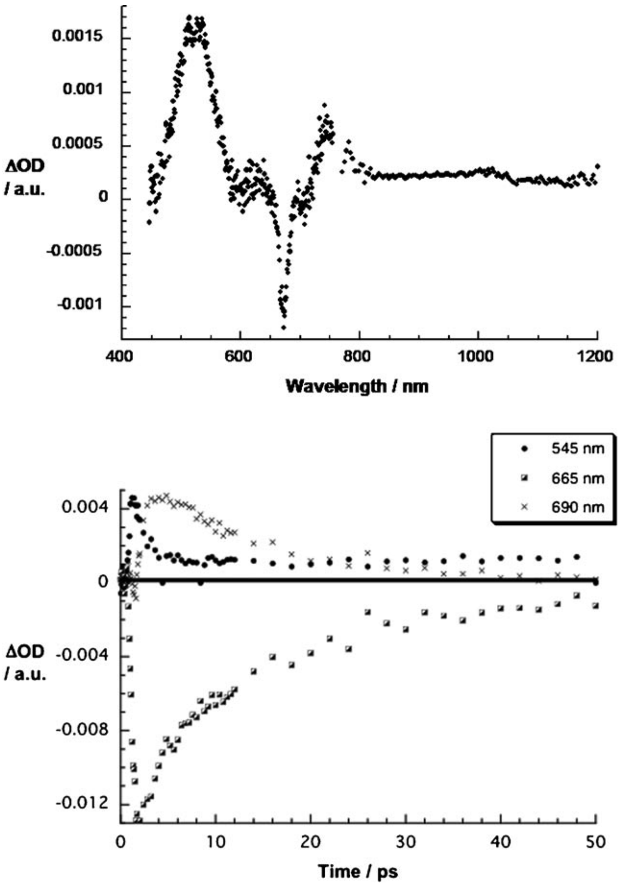


Figure 9. Upper part: differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (387 nm) of **1b** in nitrogen-saturated toluene with a time delay of 50 ps at room temperature. Lower part: time-absorption profiles of the spectra shown above at 545, 665, and 690 nm monitoring the excited-state formation and deactivation.

(i.e., **1a**) is given in Figure S12 in the Supporting Information. Implicit is that the selective excitation of the [Ln^{III}(Pc)(Pc′)] moieties in dyads **1a**–**c** is an insufficient means to power a charge transfer reaction, although being thermodynamically feasible. It is mainly the short lifetimes of the excited states of the [Ln^{III}(Pc)(Pc′)] double-decker components that bring about alternative deactivation mechanisms.

The latter argument led us to focus on the excitation of C_{60} in the [Ln^{III}(Pc)(Pc′)]–C_{60} conjugates **1a**–**c**. Notable is the singlet excited state lifetime of C_{60} (i.e., 1.4 ns). Therefore, we turned to 387 nm excitation, which excites, nevertheless, both C_{60} and [Ln^{III}(Pc)(Pc′)] components. In line with this assumption is the fact that the doublet excited state features of the [Ln^{III}(Pc)(Pc′)] moieties are discernable in the spectra of **1a**–**c**. In Figure 9 (i.e., dyad **1b**) the minima are seen at 460, 600, 675, and 900 nm, while at 555, 630, 705, and 955 nm new maxima develop. In addition, a broad transition around 880 nm, which correlates with the singlet excited state of C_{60}, seems to be superimposed to the aforementioned [Ln^{III}(Pc)(Pc′)] features. Commencing with the disappearance of [Ln^{III}(Pc)(Pc′)]-centered excited states at about 20 to 30 ps, the charge-separated state features start to evolve, namely, the fingerprint absorption of one-electron reduced C_{60} at 1010 nm. On the other hand, oxidation of the [Ln^{III}(Pc)(Pc′)] component in conjugates **1a**–**c** is implied by the new maxima at 515 nm and 760 nm and confirmed by electrochemical and radiolytical assays—see Figure 10. No notable decay is seen for the newly formed

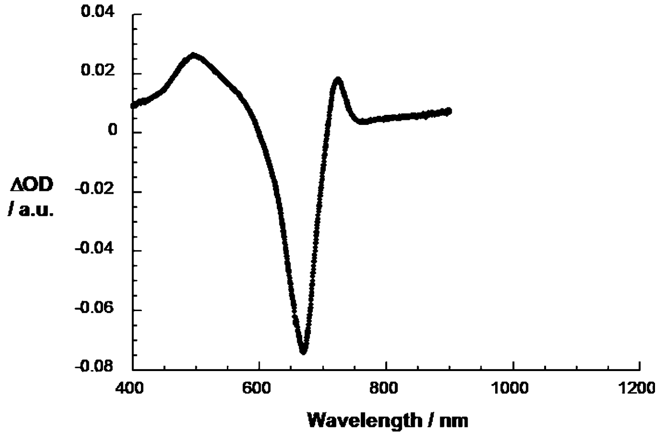


Figure 10. Spectroelectrochemical oxidation of **1b** in nitrogen-saturated toluene at an applied potential of +0.6 V.

charge separated state on the timescale of the femtosecond experiments, that is, 3 ns, which suggests an upper limit for lifetime of >3 ns in toluene.

Conclusions

We have prepared a series of novel lanthanide(III) bis(phthalocyaninato)–C_{60} complexes **1a–c.** The synthetic strategy towards **1a–c** consisted in the preparation of heteroleptic lanthanide(III) bis(phthalocyaninatos) **3a–c**, which have one unsubstituted Pc ring and another one unsymmetrically functionalized with six solubilizing moieties and one reactive position (i.e., a primary alcohol). Therefore, the esterification reaction of these unsymmetric double-deckers with a carboxylic acid containing fullerene derivative (**2**) affords $[Ln^{III}(Pc)(Pc')]$–C_{60} conjugates **1a–c** in reasonable yields. The solution electrochemistry for all these dyads shows one double-decker-based oxidation process and six reduction ones, which are centered either on the C_{60} or on the $[Ln^{III}(Pc)(Pc')]$ unit. Owing to the radical nature of the $[Ln^{III}(Pc)(Pc')]$ component in dyads **1a–c**, the first reduction wave corresponds to the first reduction of the double-decker component, that is, putting a second electron in its SOMO. As a consequence, the electrochemical molecular band gap for these $[Ln^{III}(Pc)(Pc')]$–C_{60} conjugates (ranging from 0.61 V for **1c** to 0.72 V for **1a**) corresponds to the potential difference between the first reduction of the $[Ln^{III}(Pc)(Pc')]$ moiety (namely, the first oxidation of the reduced $[Ln^{III}(Pc)(Pc')]^-$ form) and the first reduction of the C_{60} addend, that is, the second reduction process in **1a–c**. In light of their electron donor–acceptor character and the thermodynamic feasibility for the formation of the charge-separated state, we probed **1a–c** in their free-radical forms in a series of steady-state and time-resolved photophysical assays. Photoexcitation of C_{60} (387 nm) in **1a–c** leads to a rapid (i.e., ≈ 30 ps) and long-lived (i.e., beyond our time resolution of 3 ns) charge transfer. In contrast, the short-lived nature of the $[Ln^{III}(Pc)(Pc')]$ excited states fails to trigger analogous charge-transfer reactions. This result stands, however, in stark contrast to the photophysical behavior of related self-assembled ZnPc binuclear derivatives that are non-covalently linked to a C_{60} moiety; in this system, it is only the ZnPc triplet excited state that triggers a photoinduced charge transfer.[32]

Experimental Section

General methods: Chemicals were purchased from commercial suppliers and used without further purification. 4-(1′-octyl-3′,4′-fulleropyrrolidin-2′-yl)benzoic acid[24] and 2,3,9,10,16,17-hexa-(*p-tert*-butylphenoxy)-23-(*p*-hydroxymethyl)phenyl-phthalocyanine[23] were prepared using described procedures. Column chromatography was carried out on silica gel (Merck, Kieselgel 60, 230–400 mesh, 60 Å), and TLC, on aluminium sheets precoated with silica gel 60 F_{254} (E. Merck). Size exclusion chromatography was carried out on Bio-Beads S-X1 (200–400 mesh). Elemental analyses were performed with a Perkin–Elmer 2400 CHN equipment. Melting points were determined in a Büchi 504392-S equipment and are uncorrected. IR spectra were recorded on a Bruker Vector 22 spectrophotometer using KBr disks. MALDI-TOF-MS spectra were determined on a BRUKER REFLEX III instrument equipped with a nitrogen laser operating at 337 nm. NMR spectra were recorded with a Bruker AC-300 instrument. UV/vis spectra were recorded with a Hewlett–Packard 8453 instrument.

Electrochemistry: Electrochemical measurements were performed at room temperature in a potentiostate/galvanostate Autolab PGSTAT30. Measurements were carried out in a home-built one-compartment cell with a three-electrode configuration, containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as supporting electrolyte. A glassy carbon (GCE) was used as the working electrode, a platinum wire as the counter electrode and, a $Ag/AgNO_3$ non-aqueous electrode was used as reference. Prior to each voltammetric measurement the cell was degassed under an argon atmosphere for about 20 min. The solvent, THF, was freshly distilled from Na. The electrochemical measurements were performed by using a concentration of approximately 0.2 mM of the corresponding compound, and ferrocene was added as an internal reference.

Photophysics: Steady-state emission spectra were recorded on a FluoroMax 3 fluorometer (vis detection) and on a Fluorolog spectrometer (NIR detection). Both spectrometers were built by HORIBA JobinYvon. The measurements were carried out at room temperature. Femtosecond transient absorption studies were performed with 665 nm and 387 nm laser pulses (1 kHz, 150 fs pulse width) from an amplified Ti:Sapphire laser system (Clark-MXR, Inc.), the laser energy was 200 nJ.

Pulse radiolysis: Pulse radiolysis experiments were performed by using 50 ns pulses of 15 MeV electrons from a linear electron accelerator (LINAC). Dosimetry was based on the oxidation of SCN^- to $(SCN)_2^{\bullet -}$, which in aqueous, N_2O-saturated solution takes place with $G \approx 6$ (*G* denotes the number of species per 100 eV, or the approximate μM concentration per 10 J absorbed energy). The radical concentration generated per pulse was varied between $(1–3) \times 10^{-6}$ M.

Spectroelectrochemistry: All the experiments were performed with a home-built cell and a three-electrode setup: a light-transparent platinum gauze as working electrode, a platinum wire as counter electrode, and a silver wire as quasi reference electrode. Potentials were applied and monitored with an EG&G Princeton Applied Research potentiostat (model 263 A). The spectra were recorded with a UV/Vis/NIR-spectrometer Cary 5000 (VARIAN). The pathlength of the cell was determined to 2.3 mm. The results are finally shown as differential spectra, that is, the difference between a spectrum with and without an applied potential.

Standard procedure for the synthesis of $[Ln^{III}(Pc)(Pc')]$ (Ln = Sm, Eu, Lu) (3a–c): A mixture of **5**,[23] DBU and $[Ln(acac)_3]\cdot n H_2O$ in *o*-DCB was heated at 170 °C for 1.5 h under a slow stream of argon. The resulting green solution was cooled to room temperature, and the volatiles were removed under reduced pressure. The residue was washed with hexane to give intermediates $[Ln^{III}(acac)(Pc)]$ **4a–c**, which were then reacted with 1,2-dicyanobenzene and DBU in *o*-DCB/1-pentanol (1:1) for 3.5 h at 160 °C. The resulting blue solution was cooled to room temperature, and reduced to dryness. The blue solid was washed with hexane, poured onto a silica gel column and eluted with chloroform. Repeated chromatography followed by recrystallization from MeOH afforded pure $[Ln^{III}(Pc)(Pc')]$.

$[Sm^{III}(Pc)(Pc')]$ (3a): H_2Pc **5**[23] (100 mg, 0.06 mmol), DBU (1 drop), and $[Sm(acac)_3]\cdot n H_2O$ (34 mg, 0.07 mmol) in *o*-DCB (4 mL) gave [Sm(acac)(Pc)] (**4a**), which was reacted with 1,2-dicyanobenzene (34 mg, 0.26 mmol) and DBU (1 drop) in *o*-DCB/1-pentanol (1:1) (6 mL) to yield 33 mg of a green solid (23 %). M.p. >300 °C; ^1H NMR (300 MHz, $[D_7]DMF/CCl_4/N_2H_4$): $\delta = 8.5–8.4$ (m, 8H; H-α), 8.3–8.2 (m, 8H; H-α′), 8.04 (d, $J = 8.3$ Hz, 1H; H-β′), 7.9–7.7 (m, 24H; H-β, H-phenyl), 7.5–7.3 (m, 12H; H-phenyl, H-AA′BB′), 4.94 (s, 2H; CH_2OH), 1.6–1.5 ppm (m, 54H; $C(CH_3)_3$); MS (MALDI, dithranol): *m/z*: 2167–2177; UV/Vis ($CHCl_3$): λ_{max} (log ε) = 913 (3.5), 681 (5.4), 613 (4.8), 489 (4.6), 326 nm (5.3); FT-IR (KBr) : $\tilde{\nu} = 2959$, 2904, 2866, 1598, 1507, 1486, 1444, 1392, 1363, 1318, 1292, 1265, 1216, 1178, 1113, 1094, 1061, 1038, 1023, 1014, 883, 830, 813, 779, 755, 731 cm^{-1}.

[Eu^{III}(Pc)(Pc′)] (3b) : H_2Pc **5**[23] (100 mg, 0.06 mmol), DBU (1 drop), and [Eu(acac)$_3$]·nH$_2$O (34 mg, 0.07 mmol) in *o*-DCB (4 mL) gave [Eu(acac)(Pc)] (**4b**), which was reacted with 1,2-dicyanobenzene (34 mg, 0.26 mmol) and DBU (1 drop) in *o*-DCB/1-pentanol (1:1) (6 mL) to yield 30 mg of a green solid (21 %). M.p. >300 °C; ^{1}H NMR (300 MHz, [D$_7$]DMF/CCl$_4$/N$_2$H$_4$): $\delta = 11.4$ (s, 8H; H-α), 11.32 (s, 1H; H-α′), 11.09 (s, 1H; H-α′), 11.00 (s, 1H; H-α′), 10.99 (s, 1H; H-α′), 10.96 (d, $J = 7.8$ Hz, 1H; H-α′), 10.88 (s, 1H; H-α′), 10.83 (s, 1H; H-α′), 10.75 (s, 1H; H-α′), 9.46 (d, $J = 7.8$, 1H; H-β′), 9.3–9.2 (m, 8H; H-β), 8.8–8.4 (m, 28H; H-phenyl, H-AA′BB′), 5.34 (s, 2H; C*H*$_2$OH), 1.6–1.5 ppm (m, 54H; C(CH$_3$)$_3$); MS (MALDI, dithranol): *m/z*: 2171–2177; UV/Vis (CHCl$_3$): λ_{max} (log ε) = 915 (3.5), 679 (5.4), 612 (4.8), 486 (4.6), 326 nm (5.3); FT-IR (KBr) : $\tilde{\nu} = 2958$, 2360, 2341, 1598, 1507, 1486, 1444, 1392, 1362, 1318, 1291, 1264, 1215, 1176, 1113, 1093, 1034, 1023, 1013, 922, 883, 829, 779 cm^{-1}.

[Lu^{III}(Pc)(Pc′)] (3c) :H_2Pc **5**[23] (120 mg, 0.08 mmol), DBU (1 drop), and [Ln(acac)$_3$]·nH$_2$O (31 mg, 0.09 mmol) in *o*-DCB (4 mL) gave [Lu(acac)(Pc)] (**4c**), which was reacted with 1,2-dicyanobenzene (41 mg, 0.32 mmol) and DBU (1 drop) in *o*-DCB/1-pentanol (1:1) (6 mL) to yield 33 mg of a green solid (19 %). M.p. >300 °C; ^{1}H NMR (300 MHz, [D$_7$]DMF/CCl$_4$/N$_2$H$_4$): $\delta = 9.4$–9.3 (m, 6H; H-α), 9.19 (s, 1H; H-α′), 9.1–9.0 (m, 2H; H-α), 8.97 (d, $J = 7.9$ Hz, 1H; H-α′), 8.75 (s, 1H; H-α′), 8.74 (s, 1H; H-α′), 8.7–8.6 (m, 4H; H-α′), 8.4–8.2 (m, 8H; H-β), 8.04 (d, $J = 7.9$ Hz, 1H; H-β′), 8.0–7.9 (m, 16H; H-phenyl), 7.8–7.7 (m, 12H; H-phenyl, H-AA′BB′), 5.04 (s, 1H; C*H*$_2$OH), 1.8–1.6 ppm (m, 54H; C(CH$_3$)$_3$); MS (MALDI, dithranol): *m/z*: 2194–2200; UV/Vis (CHCl$_3$): λ_{max} (log ε) = 922 (3.2), 668 (5.5), 603 (4.7), 463 (4.6), 322 nm (5.3); FT-IR (KBr) : $\tilde{\nu} = 2956$, 2865, 1718, 1644, 1604, 1507, 1480, 1446, 1393, 1363, 1319, 1290, 1263, 1214, 1175, 1110, 1078, 1038, 1023, 1013, 882, 827, 752, 730 cm^{-1}.

Standard procedure for the synthesis of [Ln^{III}(Pc)(Pc′)]–C$_{60}$ (Ln = Sm, Eu, Lu) (1a–c): A mixture of **2**,[24] DMAP, and DCC in dry THF was reacted at 0 °C for 20 min. Then, the corresponding lanthanide bis(phthalocyaninato) **3a–c** was added, and the mixture was stirred for two days at room temperature. After that, the solvent was removed under reduced pressure, hexane was added and the mixture was filtrated. The residue was first purified by size exclusion chromatography (THF) and then by column chromatography on silica gel using chloroform as eluent. Repeated chromatography followed by recrystallization from MeOH afforded pure [Ln^{III}(Pc)(Pc′)]–C$_{60}$ dyads **1a–c**.

[Sm^{III}(Pc)(Pc′)]-C$_{60}$ (1a) : Compound **2**[24] (30 mg, 0.03 mmol), DMAP (6 mg, 0.03 mmol), DCC (30 mg, 0.03 mmol), and **3a** (60 mg, 0.03 mmol) in THF (10 mL) yielded 48 mg of a green solid (52 %). M.p. >300 °C; ^{1}H NMR (300 MHz, [D$_7$]DMF/CCl$_4$/N$_2$H$_4$): $\delta = 8.6$–8.4 (m, 8H; H-α), 8.3–8.2 (m, 8H; H-α′), 8.0–7.8 (m, 25H; H-β, H-β’, H-phenyl), 7.5–7.3 (m, 12H; H-phenyl, H-AA′BB′), 1.7–1.4 ppm (m, 54H; C(CH$_3$)$_3$); MS (MALDI, dithranol): *m/z*: 3144–3156, 2430 [$M-$C$_{60}$]$^+$; UV/Vis (CHCl$_3$): λ_{max} (log ε) = 914 (3.0), 681 (5.0), 615 (4.5), 489 (4.3), 326 nm (5.1); FT-IR (KBr) : $\tilde{\nu} = 3423$, 2960, 2926, 2865, 1713, 1607, 1508, 1481, 1448, 1394, 1364, 1319, 1263, 1217, 1176, 1091, 1023, 883, 804, 731 cm^{-1}.

[Eu^{III}(Pc)(Pc′)]-C$_{60}$ (1b) : Compound **2**[24] (30 mg, 0.03 mmol), DMAP (6 mg, 0.03 mmol), DCC (30 mg, 0.03 mmol), and **3b** (60 mg, 0.03 mmol) in THF (10 mL) yielded 48 mg of a green solid (48 %). M.p. >300 °C; ^{1}H NMR (300 MHz, [D$_7$]DMF/CCl$_4$/N$_2$H$_4$): $\delta = 11.5$ (s, 8H; H-α), 11.0–10.7 (m, 8H; H-α′), 9.5 (d, $J = 7.8$ Hz, 1H; H-β′), 9.3 (s, 8H; H-β), 8.8–8.4 (m, 28H; H-phenyl, H-AA′BB′), 1.5–1.3 ppm (m, 54H; C(CH$_3$)$_3$); MS (MALDI, dithranol): *m/z*: 3148–3156, 2431 [$M-$C$_{60}$]$^+$; UV/Vis (CHCl$_3$): λ_{max} (log ε) = 914 (3.4), 679 (5.0), 612 (4.4), 485 (4.2), 326 nm (5.0); FT-IR (KBr) : $\tilde{\nu} = 3443$, 2952, 2921, 2851, 1713, 1596, 1506, 1485, 1441, 1392, 1361, 1318, 1263, 1216, 1173, 1112, 1092, 1038, 1013, 881, 828, 754, 729 cm^{-1}.

[Lu^{III}(Pc)(Pc′)]-C$_{60}$ (1c) : Compound **2**[24] (20 mg, 0.02 mmol), DMAP (3 mg, 0.02 mmol), DCC (6 mg, 0.02 mmol), and **3c** (39 mg, 0.02 mmol) in THF (10 mL) yielded 32 mg of a green solid (52 %). M.p. >300 °C; ^{1}H NMR (300 MHz, [D$_7$]DMF/CCl$_4$/N$_2$H$_4$): $\delta = 9.4$–9.3 (m, 6H; H-α), 9.2 (s, 1H; H-α′), 9.1 (s, 2H; H-α), 9.0 (s, 1H; H-α′), 8.8–8.6 (m, 6H; H-α′), 8.5–8.2 (m, 9H; H-β, H-β′), 8.1–7.9 (m, 24H; H-phenyl), 7.8–7.6 (m, 4H; H-AA′BB′), 6.0–5.3 (m, 3H; H-pyrrol), 1.8–1.5 ppm (m, 54H; C(CH$_3$)$_3$); MS (MALDI, dithranol): *m/z*: 3171–3179 [M]$^+$, 2453 [$M-$C$_{60}$]$^+$; UV/Vis (CHCl$_3$): λ_{max} (log ε) = 921 (3.0), 668 (5.4), 603 (4.6), 463 (4.5), 321 nm (5.3); FT-IR (KBr) : $\tilde{\nu} = 3423$, 2952, 2922, 2853, 2361, 1713, 1597, 1506, 1443, 1394, 1362, 1322, 1291, 1263, 1215, 1173, 1112, 1095, 1025, 1013, 883, 827, 814, 756, 732 cm^{-1}.

Benzoic acid, 4[(1′-octyl-3′,4′-fulleropyrrolidin-2′-yl]-[4″-(1‴,1‴-dimethyl-phenyl)] methyl ester (6): A mixture of compound **2**[16] (70 mg, 0.07 mmol), DCC (14 mg, 0.07 mmol), and DMAP (9 mg, 0.07 mmol) was reacted in dry THF (5 mL) at 0 °C for 20 min. Then, 4-*tert*-butyl-benzyl alcohol (12 mg, 0.07 mmol) was added and the mixture was stirred for 2 days at room temperature. After that, the solvent was removed under reduced pressure, toluene (10 mL) was added and the mixture was filtrated. The residue was purified by column chromatography on silica gel using dichloromethane as eluent. Recrystallization from MeOH yielded 42 mg (52 %) of pure **6** as a brown solid. M.p. >250 °C; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 8.12$ (d, $J = 7.9$ Hz, 2H; H-Ar), 7.9 (brs, 2H; H-Ar), 7.40 (s, 4H; H-Ar), 5.32 (s, 2H; C*H*$_2$-Ar), 5.13 (d, $J = 9.3$ Hz, 1H; CH$_2$-pyrr), 5.11 (s, 1H; CH-pyrr), 4.16 (d, $J = 9.4$ Hz, 1H; CH$_2$-pyrr), 3.1–3.0 (m, 1H; CH$_2$N), 2.6–2.5 (m, 1H; CH$_2$N), 1.9–1.8 (m, 2H; C*H*$_2$CH$_3$), 1.4–1.3 (m, 10H; CH$_2$), 1.42 (s, 9H; C(CH)$_3$)$_3$), 0.9–0.8 ppm (m, 3H; CH$_3$); ^{13}C NMR (300 MHz, CDCl$_3$): $\delta = 166.5$ (CO), 156.5, 154.3, 153.3, 153.0, 151.6, 147.5, 146.7, 146.6, 146.5, 146.4, 146.3, 146.2, 146.1, 146.0, 145.9, 145.7, 145.6, 145.5, 145.4, 145.3, 144.9, 144.8, 144.6, 144.5, 143.3, 143.2, 143.1, 142.9, 142.8, 142.7, 142.5, 142.4, 142.3, 142.2, 142.1, 142.0, 141.9, 141.7, 140.4, 140.1, 139.7, 137.2, 136.7, 136.1, 135.8, 133.1, 130.4, 130.2, 129.6, 128.5, 125.7, 82.3 (OCH$_2$), 69.2 (N*C*HC$_6$H$_4$), 67.1 (CH$_2$N), 53.4 (N*C*H$_2$CH$_2$), 34.8 (*C*(CH$_3$)$_3$), 32.1 (*C*H$_2$CH$_2$CH$_3$), 31.5 (C(*C*H$_3$)$_3$), 29.8 (CH$_2$), 29.5 (CH$_2$), 28.5 (*C*H$_2$CH$_2$N), 27.7 (*C*H$_2$CH$_2$CH$_2$N), 22.9 (CH$_3$CH$_2$), 14.4 ppm (*C*H$_3$CH$_2$); MS (MALDI, dithranol): *m/z*: 1142 [M+H]$^+$; HRMS (MALDI, dithranol): *m/z*: calcd for C$_{88}$H$_{39}$NO$_2$: 1141.2981; found: 1141.2961; UV/Vis (CHCl$_3$): λ_{max} (log ε) = 431 (2.6), 331 (sh) (4.5), 257 nm (5.1); FT-IR (KBr) : $\tilde{\nu} = 2950$, 2920, 2851, 1719, 1609, 1459, 1422, 1370, 1267, 1171, 1097, 1017, 818, 765, 710 cm^{-1}.

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