Journal of Inorganic Biochemistry 108 (2012) 216–224

Contents lists available at SciVerse ScienceDirect

Journal of Inorganic Biochemistry

journal homepage: www.elsevier.com/locate/jinorgbio

Charge separation in a covalently-linked phthalocyanine-oligo (*p*-phenylenevinylene)-C_{60} system. Influence of the solvent polarity

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ARTICLE INFO

Article history:
Received 14 August 2011
Received in revised form 14 November 2011
Accepted 14 November 2011
Available online 22 November 2011

Keywords:
Phthalocyanines
Fullerenes
Electron transfer
Photophysics
Artificial photosynthesis

ABSTRACT

A photo- and redoxactive system ZnPc-oPPV-C_{60} **2**, in which the photoexcited state electron donor – zinc phthalocyanine – and the ground state electron acceptor – C_{60} – are connected by a oligo(*p*-phenylenevinylene) (oPPV) spacer, has been synthesized in a multi-step synthesis by means of two consecutive Wadsworth–Horner–Emmons and a dipolar 1,3-cycloaddition reactions as key steps. The simpler system ZnPc-C_{60} **1** has also been prepared as a reference model for photophysical studies. In this regards, the photophysical investigations by means of fluorescence, flash photolysis, and transient-absorption spectroscopy have manifested a clear dependence between charge transfer kinetics and spatial arrangement. In both systems, intramolecular charge separation evolves from the photoexcited ZnPc and yields the $ZnPc^{\cdot+}/C_{60}^{\cdot-}$ radical ion pairs. Interestingly, the $ZnPc^{\cdot+}/C_{60}^{\cdot-}$ radical ion pair lifetimes and quantum yields are strongly impacted by the solvent polarity and the distance. To this end, maximum radical ion pair lifetimes of 2900 and 5530 ps were found in anisol for **1** and **2**, respectively.

1. Introduction

It is foreseeable that artificial photosynthetic systems that will ultimately power practical solar fuels production must be based on molecular and supramolecular assemblies [1]. In natural photosynthesis, cascades of short range energy transfer and electron transfer processes occur between well arranged bioorganic dyes [2,3]. Therein, light harvesting antenna molecules mostly based on chlorophyll capture the light and transduce the excitation energy to the photosynthetic reaction center. In order to mimetic natural photosynthesis on the molecular level, the electron transfer in a large variety of bio-inspired supermolecular and supramolecular systems in particular based on chlorophyll [4,5], porphyrins [6–10], and phthalocyanines [11–20] as electron donors and SWCNT (single wall carbon nanotubes) [1,21–23], fullerenes [24–27], quinones [28–31], and graphene [32,33] as electron acceptors have already been widely investigated by us and others.

A major goal in the development of the aforementioned systems is to identify suitable candidates for solar device applications and to gain a deeper understanding of photoinduced electron transfer processes. It is, however, indispensable to develop electron-donor/acceptor systems that efficiently harvest the solar light and that efficiently form long lived radical ion pair states. In this context, phthalocyanines (Pc) emerged as molecular building blocks for the implementation as light harvesting antennas in solar energy conversion schemes. Of particular importance is their great photostability due to the aromaticity of Pcs and their high extinction coefficients in the 700 nm range allowing an effective utilization of the red part of the solar spectrum.

Fullerenes as spherical carbon structure exhibit unique electron acceptor properties. In particular, the small reorganization energy of fullerenes in electron transfer reactions making it possible that the charge separation occurs in the normal region of the Marcus parabola, whereas the charge recombination is pushed deeply into the Marcus inverted region. Keeping these features in mind, supramolecular [34,35] and supramolecular [34,36–38] assemblies of ZnPc and C_{60} were synthesized and their photophysical properties investigated. In all of the cases, charge separation from the first singlet excited state of ZnPc to the fullerene yields one electron oxidized $ZnPc^{\cdot+}$ and the one electron reduced $C_{60}^{\cdot-}$.

Previous work has shown that the molecular architecture has a tremendous impact on the yields and the lifetimes of the radical ion pair states [34]. For example, in an electron-donor/acceptor conjugate, where ZnPc and C_{60} are directly linked to each other revealed quantum yields for the radical ion pair state formation close to unity in THF but the lifetimes were limited to 49 ps [39]. Implementing, on the other hand, a spacer between both building blocks assisted in increasing the radical ion pair state lifetime but at the costs of lower quantum yields [39]. Investigating more complex structures such as a

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doi:10.1016/j.jinorgbio.2011.11.011

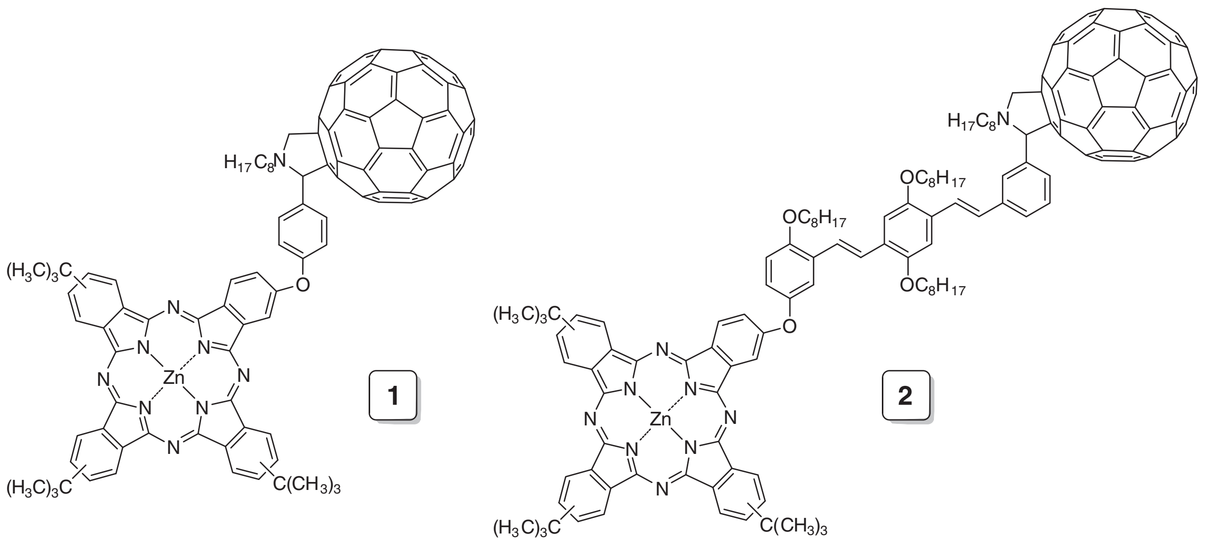
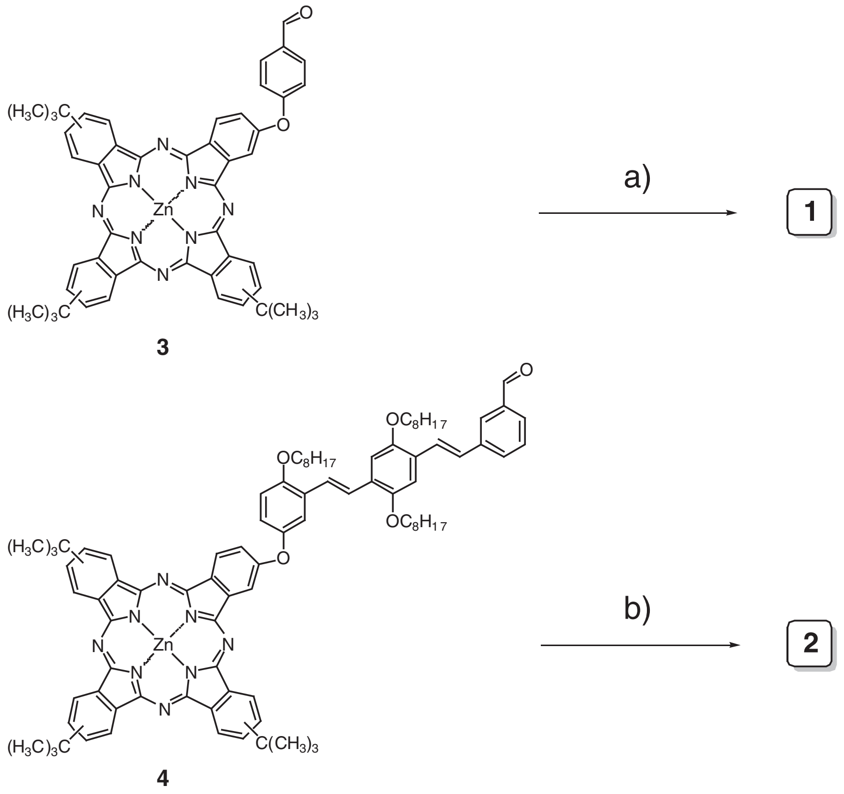


Fig. 1. Structures of phthalocyanine-based donor–acceptor systems ZnPc-C_{60} **1** and ZnPc-*o*PPV-C_{60} **2**.

tripodal relay station of ZnPcs and C_{60} [40] or a bis-C_{60}-bis-ZnPc [41] led to no appreciable changes. For example, in the former case fairly long radical ion pair state lifetimes of up to 1000 ps in benzonitrile were seen to evolve with low quantum yields of 0.28. In the latter case, the lifetimes are as short as 60 ps in anisole with quantum yields of only 0.46 what has been ascribed to the molecular arrangement of the photoactive units, whose folding favors a closer spatial distance ZnPc–C_{60} than through the direct covalent bonds.

Considerable progress was made upon implementing a [2.2] paracyclophane linker between ZnPc and C_{60}. Here, the radical ion pair state lifetime in anisole is 26000 ps, while the quantum yield reaches a value of 0.62 [42]. Finally, a phenylene-vinylene (PV) linker led to more balanced results — a lifetime of 2040 ps in anisole and a quantum yield of 0.8 [42].

In the current contribution we wish to report on the synthesis and photophysical characterization of two novel electron donor acceptor conjugates. In these electron donor acceptor conjugates ZnPc and C_{60} are linked *via* a heteroatom-containing linker in order to accelerate the charge separation and to slow down the charge recombination. One electron-donor/acceptor conjugate contains a simple oxo-phenyl linker between ZnPc and C_{60}, whereas the other was linked with an oxo-bis-PV linker (Fig. 1).



Scheme 1. Synthesis of **1** and **2**. a) *N*-octylglycine, C_{60}, toluene; 79%. b) *N*-octylglycine, C_{60}, toluene; 29%.

2. Results and discussion

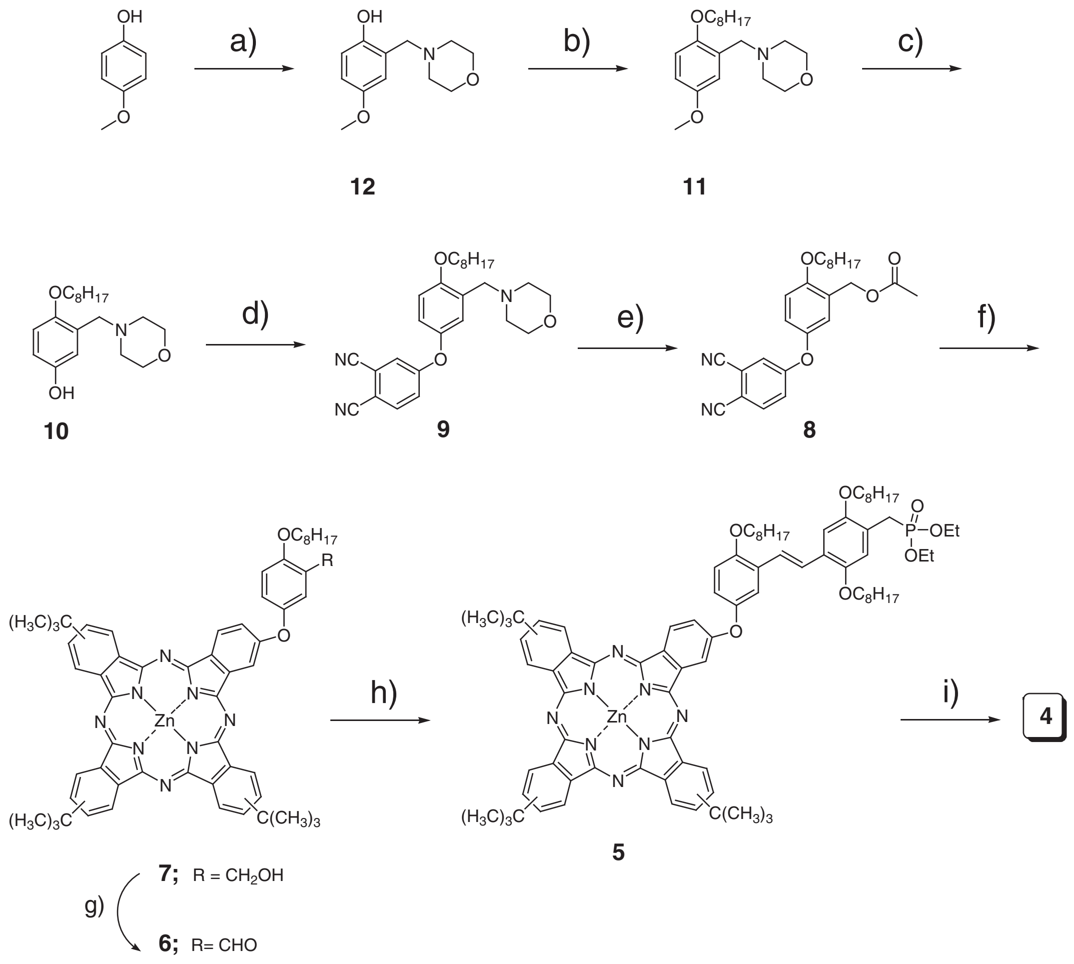
2.1. Synthesis and characterization

The syntheses of **1** and **2** were accomplished by means of 1,3-cycloaddition reactions between C_{60} and the azomethine ylides generated *in situ* upon condensation of *N*-octylglycine [43] with formylphthalocyanines **3** and **4**, respectively (Scheme 1).

Phthalocyanine **3** was prepared following a procedure described elsewhere [44], meanwhile unsymmetrical phthalocyanine **4** was obtained by using a novel synthetic procedure starting from phthalonitrile precursor **8** (Scheme 2).

To this end, phthalonitrile **8** was obtained from 4-(hydroxy)anisol after a Mannich-like reaction with *para*-formaldehyde and morpholine, followed by alkylation with tosylate **13** [45] to give intermediate **11**. Afterwards, a careful demethylation reaction with HBr, followed by an *ipso*-substitution over 4-nitrophthalonitrile in basic media, afforded phthalonitrile **9**. The substitution, in a final step, of the morpholine ring by an acetoxy group resulted in acetoxyphthalonitrile precursor **8** in a 43% overall yield. Subsequently, the unsymmetrical phthalocyanine **7** was prepared in 43% by a cyclotetramerization reaction of 4-*tert*-butylphthalonitrile and phthalonitrile **8** in a 4:1 ratio in the presence of $Zn(OAc)_2$ and refluxing dimethylaminoethanol (DMAE). The desired phthalocyanine was separated chromatographically as a mixture of regioisomers from the reaction mixture. Next, an oxidation reaction of the hydroxyl group using a very soft oxidation with the periodinane derivative IBX [46] (1-hydroxy-1,2-benziodoxole-3(1*H*)-one-1-oxide) in dimethyl sulfoxide (DMSO), as previously used by us [45], afforded formylphthalocyanine **6** in 74% yield. The synthetic route for the synthesis of **6** proceeded through a sequential two-steps Wadsworth–Horner–Emmons olefination using *t*BuOK in dry THF. First, the reaction between formylphthalocyanine **6** with 2,5-di-*n*-octyloxy-1,4-xylenebis(diethylphosphonate) [47] gave compound **5a**. In addition, the symmetrical compound ZnPc-oPPV-ZnPc **5b** was also obtained as a by-product in a non-negligible amount (22%) [48]. In a second step, the reaction of **5** with 3-(diethoxymethyl)benzaldehyde afforded, after acidic treatment, phthalocyaninic formyl derivative **4**. In both reactions, *trans*-isomers were obtained after chromatographic purification, in 42 and 47% yield, respectively. Finally in a last step, **1** and **2** were synthesized from C_{60} and *N*-octylglycine in refluxing toluene with phthalocyaninic aldehydes **3** and **4**, respectively. Isolation of the pure compounds was accomplished by column chromatography in toluene/ethyl acetate mixtures, eluting in second place after unreacted C_{60} and before double condensation by-products (bis-adducts) in 79 and 29% yields, respectively, as a mixture of unresolved regio- and enantiomers due to the surrounding *tert*-butyl groups on the phthalocyaninic core and the chiral center generated on the pyrrolidine ring, respectively.

All structures were confirmed by spectroscopic analyses (NMR, FT-IR, UV–vis. and MS). ^{1}H-NMR revealed for all phthalocyanine precursors signals in the form of multiplets between 9.8 and 6.0 ppm corresponding to the aromatic protons. Alcohol **7** also exhibited a split signal of the CH_2OH group at around 5.3 ppm, while aldehyde **6** showed the signal of the formyl group at 9.7 ppm. In the ^{1}H-NMR



Scheme 2. Synthesis of phthalocyanine **4**. a) anisol, *p*-formaldehyde, morpholine; 81%. b) (i) Cs_2CO_3, DMF, (ii) **13**, DMF; 80%. c) (i) HBr (aq), (ii) $CaCO_3$ (aq); 85%. d) 4-nitrophthalonitrile, K_2CO_3, DMF; 92%. e) $(Ac)_2O$, AcOH (glac.); 84%. f) 4-*tert*-butylphthalonitrile, $Zn(AcO)_2$, DMAE; 43%. g) IBX, DMSO; 74%. h) 2,5-di-*n*-octyloxy-1,4-xylenebis(-diethylphosphonate), *t*-BuOK, THF; 42%. i) (i) 3-(diethoxymethyl)benzaldehyde, *t*-BuOK, THF, (ii) HCl (aq) 0.1 M; 47%.

spectrum of the phthalocyanine intermediate **5** the signal of the CH_2-$P(O)(OEt)_2$ group appeared as a multiplet at around 4.5 ppm, while in HMQC-NMR the signals of the vinylic protons show up between 6.9 and 6.8 ppm with a double bond coupling constant of 16.7 Hz. These observations confirm the *trans* stereoselectivity of the Wadsworth–Emmons reaction. Furthermore, in the $^{31}P\{H\}$-NMR spectrum the P signals appeared at 26.0 ppm split in two, probably due to the regioisomers distribution. In FT-IR spectra, the $\nu_{st}(C{=}O)$ band in **6** appeared at around 1688 cm^{-1} and the $\nu_{st}(P{=}O)$ band in **5** at 1255 cm^{-1}. Moreover, **4** and **5** showed the $\nu_{oop}(C{=}C\text{-}H)$ for *trans* vinylenes at around 970 cm^{-1} [49]. Concerning the final products, the ^1H-NMR spectra of **1** and **2** exhibited the signals that correspond to the isoindol protons of the phthalocyanine core and the phenyl rings between 9.5 and 6.6 ppm. The three cyclic pyrrolidine signatures and the one from the alkyl methylene attached to the nitrogen appeared between 5.4-4.0 and 3.6 ppm, respectively. In general, **2** showed more split signals than **1** due to the higher complexity of its structure, the number of regioisomers related to the double bond, and the aggregation phenomena. In MS spectrometry (MALDI) also appeared for the titled compounds the corresponding molecular peaks as M^+ together with peaks due to the loss of C_{60}.

2.2. Photophysical studies

The electronic ground state absorption spectra of **1** and **2** (see Fig. 2) are essentially identical to that of ZnPc. In particular, a strong maximum is seen around 685 nm, which is flanked by minor maxima at 350 and 610 nm, which correspond to the Soret and Q-bands, respectively [50,51]. An additional band is seen at around 250 nm, which is a relatively good match for a C_{60} centered transition [52,53].

First inside into possible electron-donor–acceptor interactions, that is, between ZnPc and C_{60} was lent from fluorescence assays. In order to ensure comparable conditions solutions of **1**, **2**, and **ZnPc** were adjusted to exhibit the same absorption of *ca.* 0.05 at the 610 nm excitation wavelength. For **ZnPc**, we recorded a fluorescence spectrum that exhibits a strong *0-0 transition at 678 nm followed by vibrational fine structure (i.e., *0-1, *0-2, etc.) at lower energies. Important is the small energetic difference between the long-wavelength absorption and short-wavelength fluorescence of only 5 nm, which speaks for the structural rigidity of ZnPc. The quantum yields for the radiative pathway are 0.3 with an underlying lifetime – measured in time-resolved measurements – of 3.1 ns [54]. In relation to **ZnPc**, **1** and **2** revealed – see Fig. 3 and Table 1 – much lower fluorescence quantum yields with values, for example, 0.011 in **1** and 0.089 in **2** in THF. This leads us to hypothesis that additional deactivation processes – either charge transfer or energy transfer – dictate the excited state features of **1** and **2**.

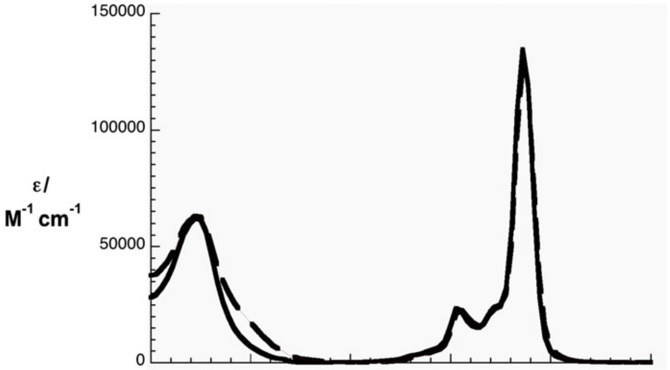


Fig. 2. Absorption spectra of **1** (solid line) and **2** (dashed line) in THF at room temperature.

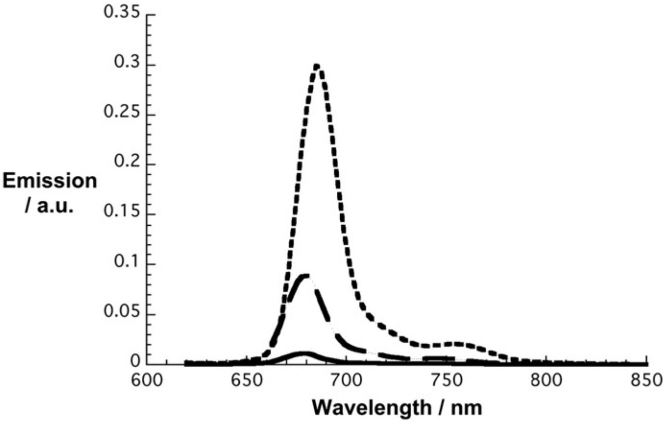


Fig. 3. Fluorescence spectra of **1** in THF (solid line), **2** in THF (dashed line), and **ZnPc** (dotted line) in toluene containing 1% pyridine at room temperature.

Transient absorption spectroscopy based on femtosecond and nanosecond laser photolysis helped to provide spectroscopic and kinetic evidence of a charge transfer mechanism between photoexcited ZnPc and C_{60}.

The transient absorption changes of **ZnPc** relate to the first singlet excited state of ZnPc showing a broad transient absorption maximizing around 490 and 800 nm, whereas a minimum at 680 nm correlates with the bleaching of Q-band absorption of the ZnPc. This transient decays *via* intersystem crossing to the first triplet excited state showing a transient absorption maximum at 500 nm. The lifetime of the first singlet excited state obtained from a monoexponential fit of the decay at 800 nm is 3.1 ns — a value that agrees well with previous reports [55,56].

When probing **1** and **2** the same singlet excited state characteristics of ZnPc were found – despite the presence of the electron accepting fullerene – upon photoexcitation. The ZnPc singlet excited state features decay much faster in **1** and **2** compared to **ZnPc** and gave rise to the formation of three new transient absorption bands maximizing at 520, 840, and 1000 nm (see Figs. 4 and 5). The maxima at 520 nm and 840 nm are assigned to the one electron oxidized form of ZnPc [57,58]. The maximum at 1000 nm, on the other hand, matches the absorption of the one electron reduced form of C_{60} [59,60].

In summary, transient absorption spectroscopy testifies the formation of radical ion pair states in **1** and **2**. The lifetimes of these radical ion pair states as obtained by fitting the decay of the 840 nm absorption tend to be longer for **2** than for **1** — see Table 2.

Finally, the quantum yields of radical ion pair state formation were determined in analogy to a previous description [39]. In particular, the values ranged from as low as 0.46 in benzonitrile for **2** to as high as 0.80 in THF for **1** — see Table 3.

In variation to previously investigated ZnPc-C_{60} conjugates [39,40] in polar and medium polar solvents (i.e., THF) the features of the radical ion pair state transform over time into those of the triplet excited state centered at ZnPc. Spectroscopic support for this conclusion came from a new transient absorption maximum at 500 nm — see Fig. 6 [56]. Both, namely the radical ion pair state decay and the triplet excited state formation are kinetically linked to each other. The triplet quantum yields were determined by measuring the singlet oxygen phosphorescence upon photoexcitation of oxygen saturated solutions

Table 1
Fluorescence quantum yields of **1** and **2** in solvents of different polarity.

	1	2
Toluene	0.033	0.064
THF	0.011	0.089
Benzonitrile	0.004	0.059

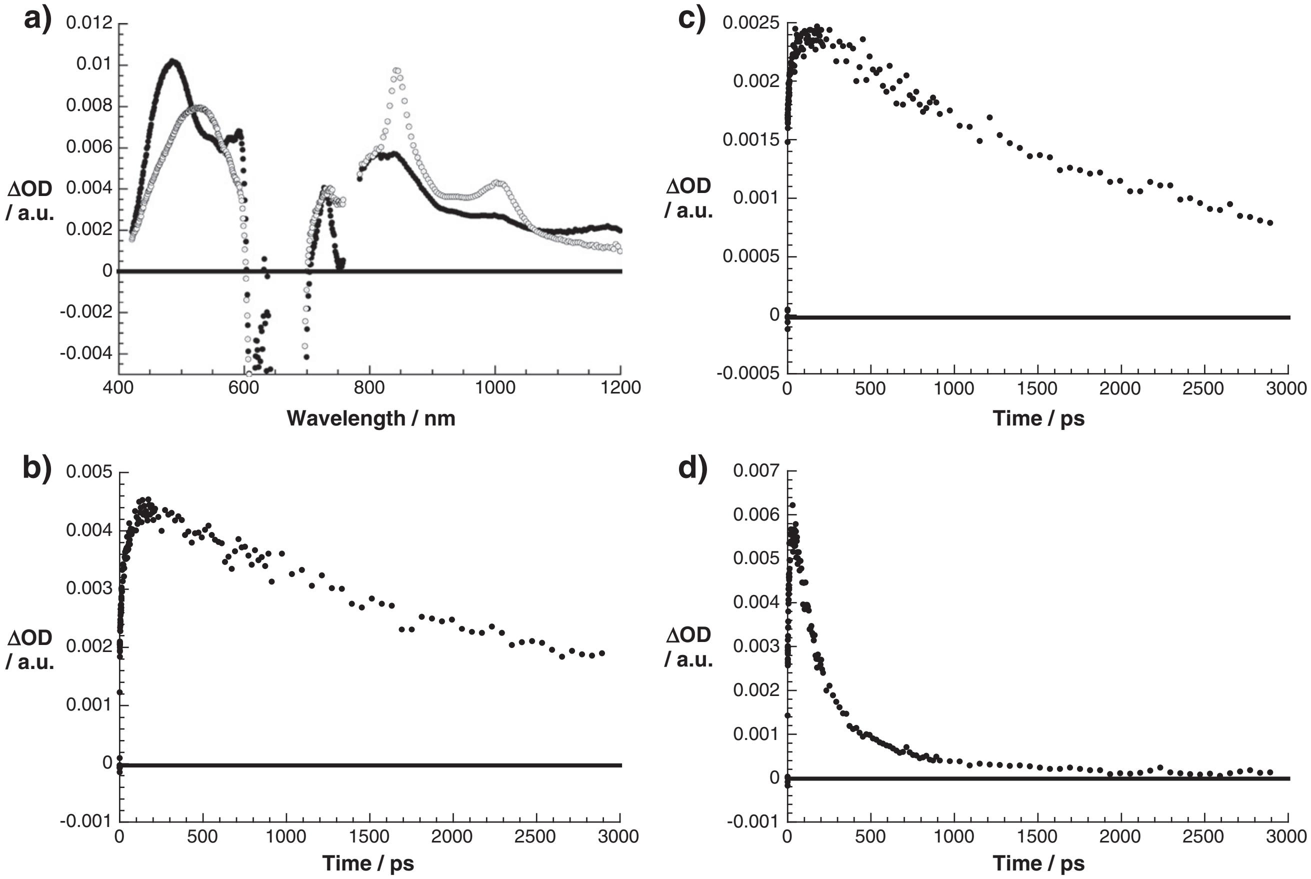


Fig. 4. (a) Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (670 nm–100 nJ) of **1** (~2.0×10^{-5} M) in argon saturated anisole with time delays of 1 (filled circles) and 102 ps (open circles) at room temperature. (b) Time absorption profile at 840 nm of the spectra shown above, monitoring the charge separation and charge recombination in anisole. (c) Time absorption profile at 840 nm monitoring the charge separation and charge recombination in THF. (d) Time absorption profile at 840 nm monitoring the charge separation and charge recombination in benzonitrile.

at 670 nm with **ZnPc** as a reference (i.e., 0.7). Quantum yields for **1** were 0.79 in toluene and 0.18 in THF, while for **2** the values were 0.79 in toluene and 0.29 in THF.

3. Conclusions

In summary, we have succeeded in the syntheses of two novel ZnPc-C_{60} electron donor acceptor conjugates bearing different linkers that both contain an oxygen atom. In addition, we have confirmed the efficient formation of long-lived radical ion pairs, that is, $ZnPc^{\cdot +}$-$C_{60}^{\cdot -}$. Most important is the fact that the incorporation of n orbitals-containing heteroatoms (i.e., oxygen) facilitates, on one hand, the charge separation, but slows down, on the other hand, the energy wasting charge recombination. Surprisingly high are the quantum yields of charge separation with values of 0.8 and 0.79 in THF and benzonitrile, respectively, for **1**.

4. Materials and methods

4.1. Photophysics

Optical absorptions were measured with a Cary 5000 UV/Vis–NIR spectrometer (Varian). Such measurements, with the exception of the femtosecond photolysis experiments, were carried out using quartz cells with a 1 cm optical path length. Steady-state fluorescence measurements were performed by using a Fluoromax P (Horiba Jobin Yvon). Transient absorption experiments – based on nanosecond laser photolysis – were performed with the output of the third harmonics (i.e., 355 nm) coming from a Nd:YAG laser (Brilliant, Quantel). Pulse widths of <5 ns with an energy of 10 mJ were selected. The optical detection is based on a pulsed (MSP 05, Müller Elektronik-Optik) xenon lamp (XBO 450, Osram), a monochromator (Spectra Pro 2300i, Acton Research), a R928 photomultiplier tube (Hamamatsu Photonics), a Nano 5 InGaAs photodiode (Coherent) and a 1 GHz digital oscilloscope (WavePro7100, LeCroy). The laser power of every laser pulse was registered using a bypath with a fast silicon photodiode. The solvents were always of spectroscopic grade. The ns-laser photolysis experiments were performed using 1 cm quartz cells and the solutions were saturated with argon. The femtosecond transient absorption measurements were carried out with a CPA-2101 femtosecond laser (Clark MXR). The excitation wavelength was generated with a NOPA (Clark MXR). The laser output energy was 100 nJ per pulse.

4.2. Experimental part

*4.2.1. 9,16,23-Tri-tert-butyl-2-{4′-[(3″-N-n-octyl)-[60]fulleropyrrolidin-2″-yl]phenoxy}phthalocyaninato zinc(II)} (regioisomers mixture) (**1**)*

C_{60} fullerene (255 mg, 0.354 mmol) and *N*-octylglycine (113 mg, 0.606 mmol) were dissolved in dry toluene (40 mL) in an ultrasounds bath. To this solution, a well-stirred solution of phthalocyanine **3** (100 mg, 0.101 mmol) in dry toluene (20 mL) was added dropwise. Afterwards, the mixture was refluxed for 18 h in an argon atmosphere. When cooled, the solvent was vacuum-evaporated affording a brown-greenish residue. The desired compound was purified from the crude on a chromatographic column on silica gel (SiO_2) using a

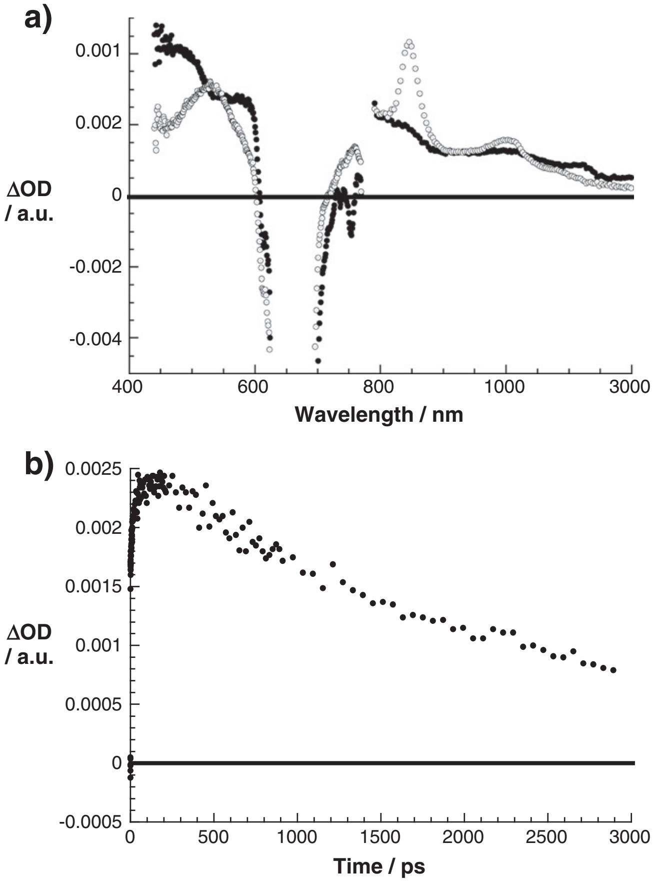


Fig. 5. (a) Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (670 nm–100 nJ) of **2** (~2.0×10^{-5} M) in argon saturated anisole with time delays of 1 (filled circles) and 102 ps (open circles) at room temperature. (b) Time absorption profile at 840 nm monitoring the charge separation and charge recombination in THF.

gradient of polarity, from toluene to toluene/ethyl acetate (20:1) as eluent. In this way, **1** 137 mg (79%) was obtained as dark green solid. Mp: >250 °C. ^{1}H-NMR (500 MHz, THF-d_6), δ = 9.5-8.7 (m, 8H; PcH), 8.2-8.0 (m, 4H; PcH), 8.0-7.3 (m, 4H; ArH), 5.38 (m, 1H; C$\underline{H}$NCH$_2$), 4.98 (m, 1H; CHNC$\underline{H}_2$), 4.09 (m, 1H; CHNC$\underline{H}_2$), 3.37 (m, 2H, NCH$_2$), 2.3-0.8 [m, 42H, (CH$_2$)$_6$CH$_3$, C(CH$_3$)$_3$]. UV–vis (THF), λ_{max} (log ε) = 673 (5.4), 608 (4.6), 348 (5.0), 240 (5.1) nm. MS (MALDI, dithranol), m/z = 1717–1709 [M]$^+$ (42%), 996–989 [M-C$_{60}$]$^+$ (100%). HRMS (MALDI-TOF, dithranol): calc. for C$_{120}$H$_{63}$N$_9$OZn: 1709.44812, found: 1709.44415.

4.2.2. 4-Methoxy-2-(morpholino-N-methyl)phenol (*12*)

A mixture of anisol (1.00 g, 8.06 mmol), *p*-formaldehyde (242 mg, 8.42 mol) and morpholine (702 mg, 8.06 mol) in benzene (22 mL) was refluxed in a Dean–Stark equipped set for 18 h. After cooling, the solvent was vacuum-evaporated affording a dark oily orangish residue. The crude was dissolved in CHCl$_3$, washed with water (4×60 mL), a 10% bisulphite solution (2×50 mL) and brine (2×50 mL). After drying over Na$_2$SO$_4$, the solvent was eliminated and the crude subjected to chromatography on silica gel with toluene/ethyl acetate (3:2) as eluent, yielding **12** (1.46 g, 81%) as an yellow-orangish oil. ^{1}H-NMR (200 MHz, CDCl$_3$), δ = 9.87 (br s, 1H; ArO$\underline{H}$), 6.77-6.74 (m, 2H, H-3, H-5), 6.56 (br d, 1H; H-2), 3.75 [br t, 4H; N(CH$_2$)$_2$(C$\underline{H}_2$)$_2$O], 3.74 (s, 3H; ArOCH$_3$), 3.66 (s, 1H; ArC$\underline{H}_2$N), 2.56 [br t, 4H; N(C$\underline{H}_2$)$_2$(CH$_2$)$_2$O]. ^{13}C-NMR (75 MHz, CDCl$_3$), δ = 152.6 (C-4), 151.2 (C-1), 121.3 (C-2), 116.5 (C-6), 114.7 (C-3), 113.8 (C-5), 66.7 (NCH$_2\underline{C}$H$_2$O), 61.9 (ArOCH$_3$), 55.7 (ArCH$_2$N), 52.9 (N$\underline{C}$H$_2$CH$_2$O). MS (EI): m/z = 223 [M]$^+$ (87%), 208 M$_1$ [M-CH$_3$]$^+$ (7%), 136 M$_2$ [M-C$_4$H$_8$NO]$^+$ (100%), 108 M$_3$ [M$_1$-C$_5$H$_{10}$NO]$^+$ (29%), 86 [C$_4$H$_8$NO]$^+$ (67%).

Table 2
Radical ion pair state lifetimes of **1** and **2** in solvents of different polarity.

	1	2
Anisole	2900 ps	5530 ps
THF	890 ps	3410 ps
Benzonitrile	220 ps	230 ps

Table 3
Radical ion pair state quantum yields of **1** and **2** in solvents of different polarity.

	1	2
Anisole	0.56	0.55
THF	0.80	0.50
Benzonitrile	0.79	0.46

4.2.3. 1-(2-Ethylhexyloxy)-4-methoxy-2-(morpholino-N-methyl)benzene (*11*)

Compound **12** (1.40 g, 6.27 mmol) and Cs$_2$CO$_3$ (6.13 g, 18.81 mmol) in dry DMF (75 mL) were heated at 70 °C under argon atmosphere for 15 min. Subsequently, a solution of sulphonate derivative **13** (2.00 g, 7.00 mmol) in dry DMF (5 mL) was added dropwise. Then, the reaction was brought to 55 °C and stirred for 6 h. After cooling down at room temperature, the mixture was poured into brine (300 mL) and extracted with diethyl ether (4×50 mL). The organic extract was dried over Na$_2$SO$_4$, filtered and the solvent eliminated in

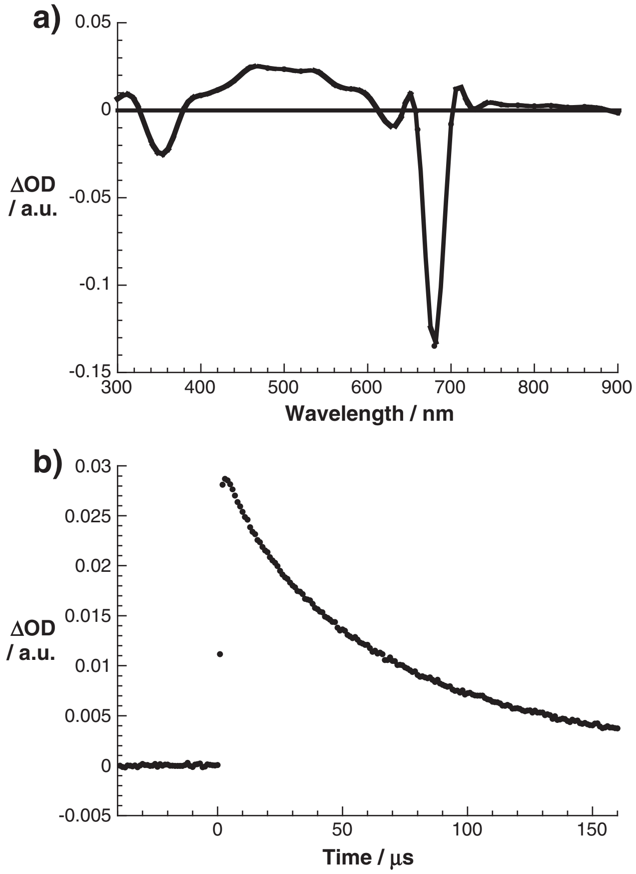


Fig. 6. (a) Differential absorption spectra (visible and near-infrared) obtained upon nanosecond flash photolysis (355 nm) of **2** (~1.3×10^{-5} M) in argon saturated toluene with a time delays of 2 µs at room temperature. (b) Time absorption profile at 500 nm of the spectrum shown above, monitoring the decay of the triplet first excited state in toluene.

vacuum. The pure compound was isolated from the brown oily residue by column chromatography (SiO_2) passing from hexane/ethyl acetate (1:1) into ethyl acetate. Following this procedure compound **11** (1.69 g, 80%) afforded as an orangish oil. ^1H-NMR (200 MHz, $CDCl_3$), $\delta = 6.97$ (d, $J_{m,3-5} = 2.9$ Hz, 1H; H-3), 6.79 (d, $J_{o,5-6} = 8.7$ Hz, 1H; H-6), 6.73 (dd, $J_{o,5-6} = 8.7$, $J_{m,3-5} = 2.9$ Hz, 1H; H-5), 3.79 (d, $J = 5.1$ Hz, 2H; $ArOCH_2$), 3.77 (s, 3H; $ArOCH_3$), 3.71 [br t, $J = 4.6$ Hz, 4H; $N(CH_2)_2(C\underline{H}_2)_2O$], 3.53 (s, 2H; $ArC\underline{H}_2N$), 2.50 [m, $J = 4.6$ Hz, 4H; $N(C\underline{H}_2)_2(CH_2)_2O$], 1.70 (st, $J = 5.8$ Hz, 1H; $ArOCH_2C\underline{H}$), 1.58-1.22 [m, 8H; $(CH_2)_4$], 0.92 (t, $J = 7.6$ Hz, 3H; CH_3), 0.87 (t, $J = 6.6$ Hz, 3H; CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$), $\delta = 153.3$ (C-4), 151.8 (C-1), 127.4 (C-2), 116.5 (C-6), 112.4 (C-3), 112.3 (C-5) 71.0 ($ArOCH_2$), 67.1 ($NCH_2\underline{C}H_2O$), 56.5 ($ArOCH_3$), 55.7 ($ArCH_2N$), 53.6 ($N\underline{C}H_2CH_2O$), 39.7 ($ArOCH_2\underline{C}H$), 30.7 (CH_2), 29.1 (CH_2), 24.1 (CH_2), 23.1 (CH_2), 14.1 (CH_3), 11.2 (CH_3). MS (EI): $m/z = 335$ $[M]^+$ (22%), 250 M_2 $[MH\text{-}C_4H_8NO]^+$ (24%), 236 M_3 $[MH\text{-}C_5H_{10}NO]^+$ (43%), 223 M_4 $[MH\text{-}C_8H_{17}]^+$ (50%), 137 M_5 $[C_8H_{17}]^+$ (100%), 86 M_6 $[C_4H_8NO]^+$ (68%).

*4.2.4. 4-(2-Ethylhexyloxy)-3-(morpholino-N-methyl)phenol (**10**)*

A heterogeneous mixture of **11** (3.30 g, 9.84 mmol) in a 45% aqueous solution of HBr was heated at 95 °C for 4 h. Once demethylation was complete, the mixture was cooled at 0 °C and a saturated solution of $CaCO_3$ was added drop by drop until pH = 9.0. Then, the suspension was poured into water (100 mL) and extracted with AcOEt (3 × 50 mL), dried over Na_2SO_4 and the solvent vacuum-eliminated after filtering. The oily brownish residue was purified by column chromatography on silica gel using toluene/ethyl acetate (1:1) as eluent, affording **10** (2.69 g, 85%) as an orangish oil. ^1H-NMR (200 MHz, $CDCl_3$), $\delta = 6.88$ (d, $J_m = 2.7$ Hz,1H; H-2), 6.74 (d, $J_o = 8.1$ Hz, 1H; H-5), 6.67 (dd, $J_m = 2.7$ Hz, $J_o = 8.1$ Hz, 1H; H-6), 3.78 (d, $J = 5.4$ Hz, 2H; $ArOCH_2$), 3.72 [br t, $J = 4.8$ Hz, 4H; $N(CH_2)_2(C\underline{H}_2)_2O$], 3.51 (s, 1H; $ArC\underline{H}_2N$), 2.51 [m, 4H; $N(C\underline{H}_2)_2(CH_2)_2O$], 1.68 (st, $J = 8.9$ Hz, 1H; $ArOCH_2C\underline{H}$), 1.55-1.20 [m, 8H; $(CH_2)_4$], 0.92 (t, $J = 7.5$ Hz, 3H; CH_3), 0.90 (t, $J = 4.5$ Hz, 3H; CH_3). MS (EI): $m/z = 321$ $[M]^+$ (23%), 222 M_3 $[MH\text{-}C_5H_{10}NO]^+$ (60%), 209 M_4 $[MH\text{-}C_8H_{17}]^+$ (63%), 123 M_5 $[M_4\text{-}C_4H_8NO]^+$ (92%), 86 M_6 $[C_4H_8NO]^+$ (100%).

*4.2.5. 4[4-(2-Ethylhexyloxy)-3-(morpholino-N-methyl)phenoxy] phthalonitrile (**9**)*

4-Nitrophthalonitrile (596 mg, 3.44 mmol), K_2CO_3 (1.38 g, 10.00 mmol) and **10** (920 mg, 2.86 mmol) in dry DMF (45 mL) were heated at 50 °C under an argon atmosphere for 66 h. After cooling down to room temperature, the mixture was poured into 300 mL of brine and extracted with diethyl ether (5 × 50 mL). The organic extracts were joined, washed with solutions of sodium hydroxide (0.1 M, 2 × 50 mL), sodium bicarbonate (2 × 50 mL) and brine (2 × 50 mL) and dried over magnesium sulfate. After filtration, the solvent was evaporated giving a yellow oily crude. Compound **9** was isolated on a chromatographic column (SiO_2) using toluene/ethyl acetate as eluent, affording (1.18 g, 92%) as viscous yellow oil that solidified by standing. Mp: 39–41 °C. ^1H-NMR (300 MHz, $CDCl_3$): $\delta = 7.70$ (d, $J_{o,5-6} = 9.7$ Hz, 1H; H-6), 7.22 (dd, $J_{o,5-6} = 9.7$ Hz, $J_{m,2-6} = 2.2$ Hz, 1H; H-5), 7.19 (d, $J_{m,2-6} = 2.2$ Hz, 1H; H-3), 7.13 (br s, 1H; H-2′), 6.90 (br d, 2H; 5′-H, 6′-H), 3.88 (d, $J = 4.8$ Hz, 2H; $ArOCH_2$), 3.70 [br t, 4H; $N(CH_2)_2(C\underline{H}_2)_2O$], 3.55 (s, 2H; $ArC\underline{H}_2N$), 2.49 [br t, 4H; $N(C\underline{H}_2)_2(CH_2)_2O$], 1.76 (st, 1H; $ArOCH_2C\underline{H}$), 1.64-1.23 [m, 8H, $(CH_2)_4$], 0.95 (t, $J = 7.0$ Hz, 3H; CH_3), 0.92 (t, $J = 6.5$ Hz, 3H; CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): $\delta = 162.6$ (C-1′),155.5 (C-1), 146.3 (C-4), 135.3 (C-5′),129.0 (C-6′),122.3 (C-2′),121.0 (C-2), 120.8 (C-3), 119.8 (C-5), 117.5 (CN), 115.5 (CN), 115.0 (C-3′), 112.5 (C-6), 108.3 (C-4′), 70.8 ($ArOCH_2$), 67.0 ($N(CH_2)_2(\underline{C}H_2)O$), 56.1 ($N(\underline{C}H_2)_2(CH_2)O$), 53.7 ($ArCH_2N$), 39.5 ($ArOCH_2\underline{C}H$), 30.7 ($CH_2$), 29.1 ($CH_2$), 24.1 ($CH_2$), 23.0 ($CH_2$), 14.0 ($CH_3$), 11.2 ($CH_3$). FT-IR (KBr): $\nu = 2958$, 2929, 2860, 2806, 2600, 2232 $\nu_{st}(C\equiv N)$, 1591, 1562, 1489, 1420, 1396, 1383, 1353, 1335, 1298, 1247, 1199, 1172, 1150, 1114, 1086 ν_{as}(C-O-C), 1072, 1035, 1010, 975, 930, 911, 891 ν_s(C-O-C), 867, 839, 826, 801, 766, 522 cm^{-1}. MS (EI): $m/z = 447$ $[M]^+$ (13%), 348 M_1 $[MH\text{-}C_5H_{10}NO^+]$ (78%), 335 M_2 $[MH\text{-}C_8H_{17}]^+$ (66%), 249 M_3 $[M_2\text{-}C_4H_8NO]^+$ (62%), 100 M_4 $[C_5H_{10}NO]^+$ (28%), 86 M_6 $[C_4H_8NO]^+$ (100%).

*4.2.6. 2-(2-Ethylhexyloxy)-5-(3,4-dicyanophenoxy)benzyl acetate (**8**)*

Derivative **9** (2.52 g, 5.63 mmol) was reacted in a mixture of acetic anhydride (53 mL) and glacial acetic acid (13 mL) under argon atmosphere for 14 h. When consumption of starting compound was complete, the solvents were evaporated and the residue dissolved in chloroform and washed with water (100 mL each). The organic extract was further washed with a solution of hydrochloric acid (0.1 M, 3 × 60 mL), neutralized with a saturated sodium bicarbonate solution (2 × 50 mL), washed with brine (2 × 50 mL) and dried over $MgSO_4$. The drier agent was removed by filtration and the chloroform evaporated under reduced pressure to leave a slurry brown oily, which was purified by column chromatography on silica using toluene/ethyl acetate (4:1) as eluent to give **8** (2.00 g, 84%) as a pale yellow oil that solidified by standing. Mp: 55–56 °C. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 7.70$ (d, $J_{o,5-6} = 9.7$ Hz, 1H; H-6), 7.23 (dd, $J_{o,5-6} = 9.7$ Hz, $J_{m,3-5} = 2.6$ Hz, 1H, H-5), 7.19 (d, $J_{m,3-5} = 2.6$ Hz, 1H; H-3), 7.05 (br s, 1H; H-2′), 6.97 (br d , 1H; H-6′), 6.94 (br d ,1H; H-5′), 5.15 [s, 2H; $ArC\underline{H}_2OC(O)CH_3$], 3.91 (d, $J = 5.4$ Hz, 2H; $ArOCH_2$), 2.10 [s, 3H: $OC(O)CH_3$] 1.76 (st, $J = 6.5$ Hz, 1H; $ArOCH_2C\underline{H}$) 1.64-1.23 [m, 8H; $(CH_2)_4$], 0.95 (t, $J = 7.0$ Hz, 3H; CH_3) 0.91 (t, $J = 5.6$ Hz, 3H; CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): $\delta = 170.8$ ($O\underline{C}(O)CH_3$), 162.6 (C-4), 155.1 (C-1′), 146.2 (C-4′), 135.5 (C-6), 127.0 (C-3′), 121.6 (C-5), 121.3 (C-3), 121.1 (C-2), 121.0 (C-2′), 117.6 (C-6′), 115.6 (CN), 115.2 (CN), 112.5 (C-5′), 108.5 (C-1), 70.9 ($ArOCH_2$), 61.3 ($Ar\underline{C}H_2OC(O)CH_3$), 39.5 ($ArOCH_2\underline{C}H$), 30.7 ($CH_2$), 29.2 ($CH_2$), 24.0 ($CH_2$), 23.1 ($CH_2$), 21.0 ($ArCH_2OC(O)\underline{C}H_3$), 14.2 ($CH_3$), 11.3 ($CH_3$). FT-IR (KBr): $\nu = 2932$, 2867, 2231 $\nu_{st}(C\equiv N)$, 1738 $\nu_{st}(C{=}O)$, 1610, 1588, 1566, 1486, 1451, 1427, 1413, 1379, 1362, 1314, 1278, 1237 ν_{as}(C-O), 1204, 1166, 1147, 1121, 1085, 1046, 1011, 969, 945, 918, 900, 852, 827, 774, 651, 526, 464, 443, 426 cm^{-1}. MS (EI): $m/z = 420$ $[M]^+$ (10%), 308 M_1 $[MH\text{-}C_8H_{17}]^+$ (9%), 248 M_2 $[M_1\text{-}C_2H_3O_2]^+$ (100%).

*4.2.7. 9,16,23-Tri-tert-butyl-2-[4-(2-ethylhexyloxy)-3-(hydroxymethyl)] phenoxyphthalocyaninato zinc(II) (regioisomers mixture) (**7**)*

Phthalonitrile **8** (200 mg, 0.48 mmol), 4-*tert*-butylphthalonitrile (351 mg, 1.90 mmol) and $Zn(AcO)_2$ (106 mg, 0.55 mmol) were stirred in DMAE (4 mL) and refluxed under argon atmosphere for 20 h. Then, the solution was cooled down and methanol (20 mL) was added. The mixture was refluxed again for further 2 h, and after cooling, poured into water (100 mL). The blue precipitate was collected by filtration through celite®. The resulting dark blue solid was washed with water, mixtures methanol/water (1:2) and (1:1) (100 mL each), and methanol (50 mL). Afterwards, the solid was dried and redissolved in tetrahydrofuran and purified by column chromatography (SiO_2) using hexane/dioxane (3:1) as eluent. The isolated blue solid obtained was triturated in hot hexane, filtered and dried to afford phthalocyanine **7** (202 mg, 43%) as a dark blue solid. Mp: >250 °C. ^1H NMR (500 MHz, $CDCl_3$): $\delta = 9.5$-8.4 (m, 8H; PcH), 8.3-7.4 (m, 4H; PcH), 7.1-6.0 (m, 3H, ArH), 5.4-5.1 (m, 2H; $ArC\underline{H}_2OH$), 4.0-3.7 (m, 2H; $ArOCH_2$), 2.2-0.6 [m, 42H; CH, CH_2, CH_3, $C(CH_3)_3$]. UV–vis (THF): λ_{max} (log ε) = 674 (4.9), 608 (4.1), 348 (4.4), 286 (4.0) nm. MS (MALDI, dithranol): $m/z = 1002$–994. Anal. Calcd (%) for $C_{59}H_{62}N_8O_3Zn$: C, 70.20; H, 6.28; N, 10.92. Found: C, 70.15; H, 6.21; N, 11.00.

*4.2.8. 9,16,23-Tri-tert-butyl-2-[4-(2-ethylhexyloxy)-3-formyl] phenoxyphthalocyaninato zinc(II) (regioisomers mixture) (**6**)*

To a well stirred and colorless solution of periodinane 1-hydroxy-1,2-benziodoxole-3(1*H*)-one-1-oxide (IBX) (90 mg, 0.321 mmol) in dimethyl sulfoxide (45 mL), compound **7** (200 mg, 0.201 mmol) was added at once. The solution was stirred at room temperature for 5 h. and then, poured over brine (200 mL) and extracted with diethyl ether (3×50 mL). The organic layer was separated, washed with a saturated solution of sodium bicarbonate (2×60 mL), brine (2×60 mL) and dried over sodium sulfate. After filtration of the drier agent, the solvent was evaporated and the blue solid was purified by a short column chromatography on silica gel using hexane/dioxane (4:1) as eluent, affording aldehyde **6** as dark blue solid (147 mg, 74%). Mp: >250 °C. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 9.9$-9.5 (br s, 1H; CHO), 8.9-8.0 (m, 8H; PcH), 8.0-7.4 (m, 4H; PcH), 7.4-6.3 (m, 3H; ArH), 4.0-3.7 (br d, 2H; $ArOCH_2$), 2.1-0.7 [m, 42H; CH, CH_2, CH_3, $C(CH_3)_3$]. FT-IR (KBr): $\nu = 2959$, 2918, 2864, 1688 $\nu_{st}(C{=}O)$, 1620, 1493, 1425, 1398, 1331, 1290, 1263, 1233, 1128, 1008, 1047, 926, 831, 752, 698, 540, 444 cm^{-1}. UV–vis ($CHCl_3$): λ_{max} (log ε) = 673 (5.0), 607 (4.3), 350 (4.6) nm. MS (MALDI, dithranol): $m/z = 1000$–992. Anal. Calcd (%) for $C_{59}H_{60}N_8O_3Zn$: C 71.25; H 6.08; N 11.27. Found: C 71.29; H 6.12; N 11.28.

*4.2.9. 9,16,23-Tri-tert-butyl-2-{[4′-(2-ethylhexyloxy)]-3′-[(E)-vinylen-4″-(diethylmethylphosphonate)-2″,5″-bis(n-octyloxy)]}phthalocyaninato zinc(II) (regioisomers mixture) (**5**)*

To a well-stirred solution of phthalocyanine **6** (120 mg, 0.121 mmol) and bis-phosphonate (230 mg, 0.362 mmol) in dry THF (20 mL), a suspension of potassium *tert*-butoxide (20 mg, 0.182 mmol) in dry THF (6.0 mL) was added drop by drop in an argon atmosphere. The reaction was allowed to react at the same temperature for 3 h, after which the solvent was evaporated in vacuum. The crude was subjected to a chromatographic column (SiO_2) in hexane/dioxane (3:1) as eluent, affording **5** (75 mg, 42%) as a blue-greenish solid. Mp: >250 °C. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 9.6$-9.1 (m, 7H; PcH), 8.8-8.6 (m, 1H; PcH), 8.3-8.2 (m, 3H; PcH), 7.66 (br s, 1H; ArH), 7.30 (br s, 1H; ArH), 7.1-7.0 (d, 1H; ArH), 6.90 (d, $J_{trans} = 16.7$ Hz 1H; Ar-CH=CH-Ar′), 6.80 (d, $J_{trans} = 16.7$ Hz 1H; Ar-CH=CH-Ar′), 6.27 (d, 1H; ArH), 4.8-4.3 (m, 2H; $ArC\underline{H}_2P$), 4.2-3.7 (br s, 6H; $ArOCH_2$), 3.6-3.2 [m, 4H; $P(O)(OC\underline{H}_2CH_3)_2$], 2.1-0.4 [m, 82H; $CH(CH_2)_4CH_3$, $P(O)(OCH_2C\underline{H}_3)_2$, CH, CH_2, $C(CH_3)_3$]. ^{31}P NMR (202 MHz, $CDCl_3$): $\delta = 25.99$, 26.03. FT-IR (KBr): $\nu = 2951$, 2920, 2854, 1610, 1487, 1464, 1404, 1388, 1361, 1328, 1263, 1255 $\nu_{st}(P{=}O)$, 1215, 1198, 1147, 1088, 1045 ν_{st}(P-O), 969 $\nu_{\delta\ oop}$ (C=C-H *trans*), 920, 827 ν_{st}(P-O), 746, 669, 671 cm^{-1}. UV–vis (THF): λ_{max} (log ε) = 680 (5.1), 613 (4.3), 349 (4.8) nm. MS (MALDI, dithranol): $m/z = 1481$–1473 $[M]^+$ (37%), 1000–992 $[M\text{-}(P(O)(OEt)_2\text{-}(3xC_8H_{17})]^+$ (12%). HRMS (MALDI-TOF, dithranol): calc. for $C_{87}H_{109}N_8O_7PZn$: 1472.7474, found: 1472.7443.

*4.2.10. 9,16,23-Tri-tert-butyl-2-{[4′-(2-ethylhexyloxy)-3′-{(E)-vinylen-2″,5″-bis(n-octyloxy)-4″-[(E)-vinylen-3‴-(formil)]fenil}fenil]fenoxi}] phthalocyaninato zinc(II) (regioisomers mixture) (**4**)*

To a well-stirred solution of compound **5** (58 mg, 0.039 mmol) and 3-(diethoxymethyl)benzaldehyde (16 mg, 0.077 mmol) in dry THF (6 mL), a suspension of *t*-BuOK (16 mg, 0.143 mmol) in dry THF (1.5 mL) was added drop by drop in an argon atmosphere. The reaction was allowed to react at the same temperature for 2 h, after which a 0.1 M HCl (5 mL) solution was added dropwise. The mixture was stirred for 30 min. and then extracted with Et_2O (2×30 mL). The organic extracts were joined, washed with a saturated solution of $NaHCO_3$ (2×30 mL) and dried over Na_2SO_4. After evaporation of the solvent at reduced pressure, the dark green crude was purified on a chromatographic column (SiO_2) in hexane/dioxane (3:1) as eluent, resulting **4** (27 mg, 47%) as a blue-greenish solid. Mp: >250 °C. ^{1}H NMR (500 MHz, THF-d_8): $\delta = 9.7$-9.5 (m, 1H; CHO), 9.5-8.8 (m, 8H; PcH), 8.3-8.1 (m, 4H; PcH), 8.0-6.5 (m, 13H; ArH, $Ar\text{-}C\underline{H}{=}C\underline{H}\text{-}Ar'$), 4.0-3.4 (m, 6H; $ArOCH_2$), 2.0-0.6 [m, 72H; CH, CH_2, $C(CH_3)_3$]. FT-IR (KBr): $\nu = 2966$, 2926, 2858, 1709 ν_{st} (C=O), 1612, 1493, 1425, 1398, 1333, 1254, 1227, 1146, 1092, 1051, 976 $\nu_{\delta\ oop}$ (C=C-H *trans*), 928, 833, 752, 692, 530, 461 cm^{-1}. UV–vis (THF): λ_{max} (log ε) = 680 (5.0), 613 (4.4), 407 (sh) (4.5), 348 (4.7) nm. MS (MALDI, dithranol): $m/z = 1461$–1453. HRMS (MALDI-TOF, dithranol): calc. for $C_{91}H_{104}N_8O_5Zn$: 1452.7424, found: 1452.7416.

*4.2.11. 9,16,23-Tri-tert-butyl-2-{[4′-(2-ethylhexyloxy)-3′-[(E)-vinylen-2″,5″-bis(n-octyloxy)-4″-{(E)-vinylen-3‴-[3‴′-(N-n-octyl)-[60] fulleropyrrolidin-2‴′-yl]fenil}fenil]fenoxi}phthalocyaninato zinc(II) (regioisomers mixture) (**2**)*

C_{60} fullerene (46 mg, 0.063 mmol) and *N*-octylglycine (24 mg, 0.126 mmol) were dissolved in dry toluene (12 mL) in an ultrasounds bath. To this solution, a well-stirred solution of phthalocyanine **6** (30 mg, 0.021 mmol) in dry toluene (8 mL) was added dropwise. Afterwards, the mixture was refluxed for 18 h in an argon atmosphere. After cooling down, the solvent was vacuum-evaporated affording a brown-greenish residue. The desired compound was purified from the crude on a chromatographic column (SiO_2) using a polarity gradient, passing from toluene to toluene/ethyl acetate (1:1). Following this procedure, **2** (14 mg, 29%) was obtained as dark green solid. Mp: >250 °C. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 9.5$-6.6 (m, 25H; PcH, ArH, Ar-CH=CH-Ar′), 5.33 (d, 1H; $C\underline{H}NCH_2$), 5.2-4.7 (m, 2H; $CHNC\underline{H}_2$), 4.2-3.8 (m, 6H, $ArOCH_2$), 3.8-3.5 (m, 2H; NCH_2), 2.1-0.6 [m, 87H, CH, CH_2, CH_3, $C(CH_3)_3$]. UV–vis (THF): λ_{max} (log ε) = 681 (4.8), 614 (4.0), 406 (sh) (4.3), 330 (4.8), 259 (5.1) nm. MS (MALDI, dithranol): $m/z = 2308$–2298 $[M]^+$ (35%), 1586–1578 $[M\text{-}C_{60}]^+$ (100%), 1000–992 $[M\text{-}(C_{83}H_{109}N_8O_2Zn)\text{-}(3xC_8H_{17})]^+$ (75%). HRMS (MALDI-TOF, dithranol): calc. for $C_{160}H_{123}N_9O_4Zn$: 2297.9021, found: 2297.8984.

Abbreviations

t-BuOK	Potassium *tert*-butoxide
Dithranol	1,8,9-Anthracenetriol
DMF	*N,N*-Dimethylformamide
DMAE	Dimethylaminoethanol
EI	Electron Impact
IBX	1-Hydroxy-1,2-benziodoxole-3(1*H*)-one-1-oxide
HMQC	Heteronuclear Multiple Quantum Correlation
HRMS	High Resolution Mass Spectrometry
MALDI	Matrix-Assisted Laser Desorption Ionization
Mp	Melting Point
MPc	Metallophthalocyanine
MS	Mass Spectrometry
oPPV	Oligo(*p*-phenylenevinylene)
Pc	Phthalocyanine
PV	Phenylene-vinylene
SWCNT	Single wall carbon nanotubes
THF	Tetrahydrofuran
TLC	Thin Layer Chromatography
TMS	Tetrametylsilane
TOF	Time-Of-Flight
UV–vis	Ultraviolet–visible

Acknowledgments

This work has been supported by the Spanish MICINN and MEC (CTQ2011-24187/BQU and CONSOLIDER INGENIO 2010, CSD2007-00010 Nanociencia Molecular, PLE2009-0070), and the Comunidad de Madrid (MADRISOLAR-2, S2009/PPQ/1533). Financial support by Fonds der Chemischen Industrie (FCI), Deutsche Forschungsgemeinschaft (SFB 583: Redoxaktive Metallkomplexe — Reaktivitätssteuerung durch molekulare Architekturen), and Exzellenzcluster EAM-Engineering of Advanced Materials is also acknowledged.

Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.jinorgbio.2011.11.011.

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