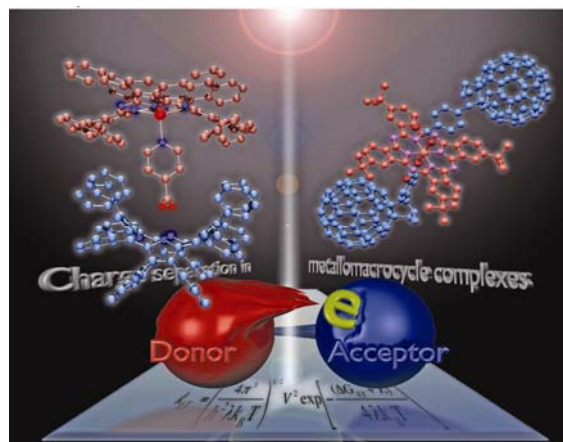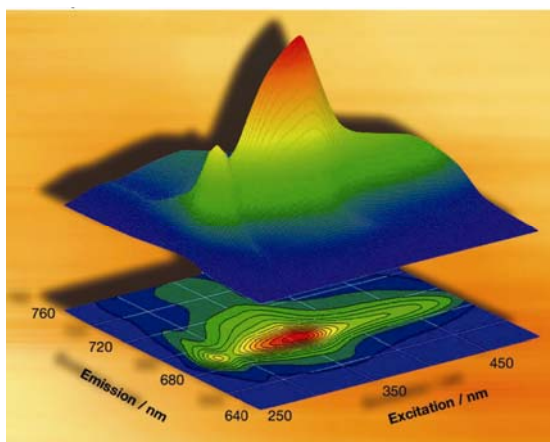**This paper is published as part of a *Dalton Transactions* themed issue on:**

Supramolecular photochemistry

Guest Editors Michael D. Ward and Julia Weinstein
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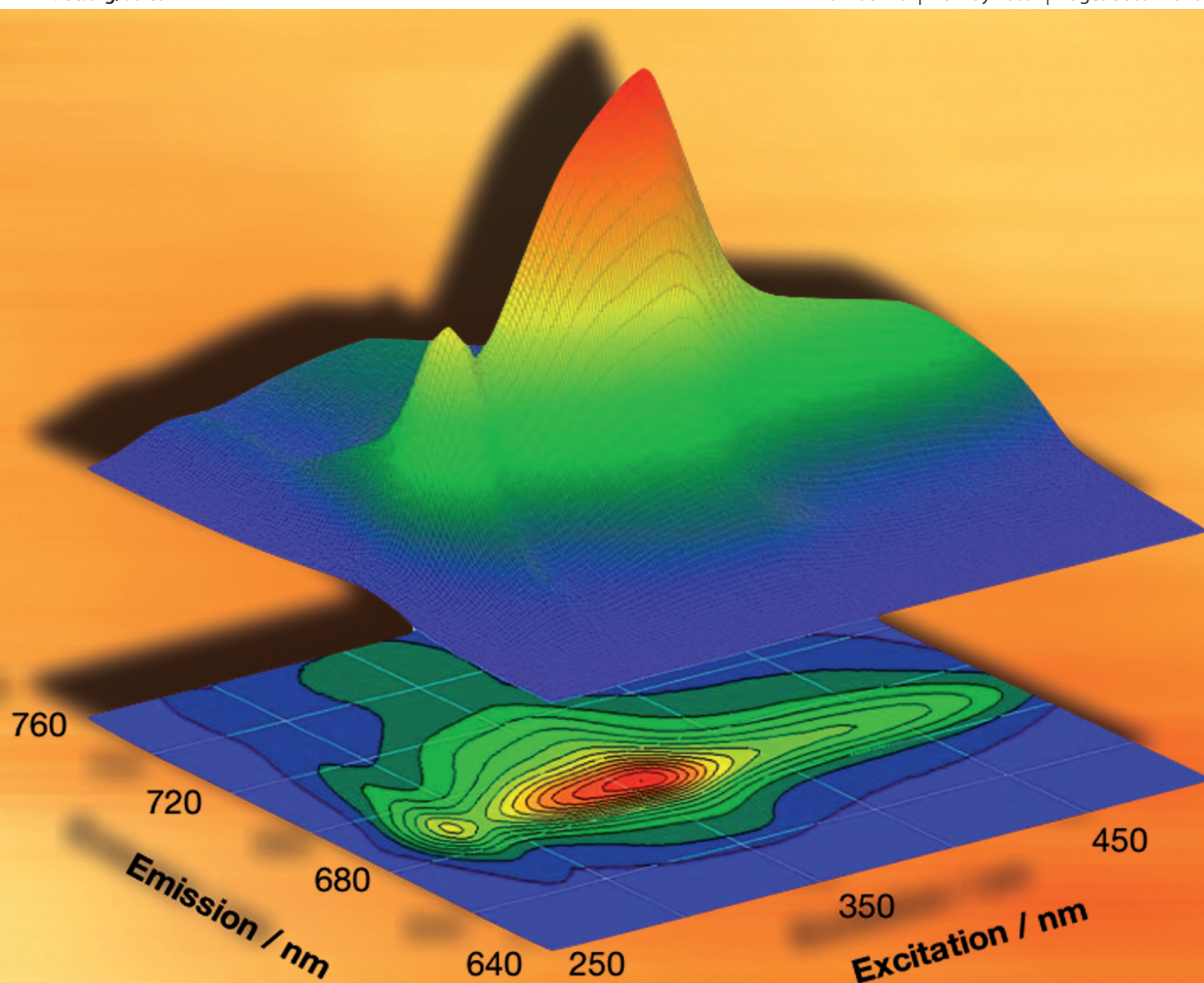
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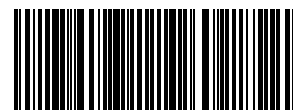
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Synthesis, photophysical and electrochemical characterization of phthalocyanine-based poly(p-phenylenevinylene) oligomers

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The synthesis of two poly(p-phenylenevinylene) oligomers (oPPV) laterally substituted by phthalocyanines (Pc) is described. The preparation of Pc-based oligomers **1** and **2** was accomplished by means of Knoevenagel and Wadsworth–Horner–Emmons reactions, respectively. Diformylphthalocyanine **3** was employed as a monomer in these reactions, thus providing functionalised conjugated oligomers upon reaction with the corresponding co-monomers, **4** and **5**. Photophysical and electrochemical experiments have been carried out with both oligomeric derivatives, revealing excited state interactions such as transduction of singlet excited state energy.

Introduction

Oligomeric and polymeric materials bearing p-phenylenvinylene substructures have shown important applications in "bulk hetero-junctions" solar cells[1] due to their tuneable photophysical properties as well as their mechanical and processing characteristics.[2] However, a mis-matched absorption of sun light and the dependence on morphology[3]—that causes phase segregation phenomena of intermixed layers[1b,d–f,h]—have prevented of obtaining of higher external quantum efficiencies and durabilities. In order to overcome these handicaps and attain control of the morphology, some improvements have consisted in the design of molecules in which the donor and acceptor moieties are chemically linked. Following these approaches, the electroactive entities covalently connected into a conjugated polymer backbone appears to be a viable way for the preparation of ambipolar conducting "double-cable" polymers (p–n type polymers).[4] This design should prevent the occurrence of phase segregation since the material is basically one molecule with two different ways (cables) for different signs of charges carrying the p–n union at molecular level.

Oligo p-phenylenevinylenes (oPPV), are one of the oligomeric architectures that have assumed a crucial importance because they work as a reference for their longer and more complex polymeric analogues.[5] Furthermore, monodisperse conjugated oligomers, eminently easier to handle and to characterize, have been acclaimed through the development of donor–acceptor arrays.[6,7]

On the other hand, phthalocyanines (Pcs) are important compounds with a plethora of applications in materials science[8] due to their unusual and non-conventional properties. Particularly, Pcs have received a enormous attention during the last years within photovoltaics field[9] due to three main reasons: (i) intense absorption of the electromagnetic radiation between 650–700 nm (Q-band, with molar extinction coefficients higher than $100\,000$ $M^{-1}cm^{-1}$), just in the area where photon flux of the AM 1.5 solar spectrum peak is maximum (around 700 nm) acting as an antenna, (ii) excellent photo-conductivities that make them promising candidates to be incorporated into donor–acceptor ensembles together with other electro or photoactive units,[10] and (iii) good photo-chemical stabilities.

Results and discussion

Oligomers **1** and **2** (Fig. 1) were prepared in the form of alternating co-polymers by condensation in basic media of diformyl derivative **3** and co-monomers **4** and **5**, respectively (Scheme 1).

The synthesis of co-monomers **4** and **5** was carried out as described elsewhere,[11] while the synthesis of phthalocyanine **3** was accomplished by using a novel route (Scheme 2) than that previously described by us for the preparation of the same compound.[12] The synthetic pathway started with a double Mannich-like reaction of 1,4-dihydroquinone with p-formaldehyde and morpholine, followed by a mono-alkylation with tosylate **11** to give intermediate **9**. A subsequent ipso-substitution of derivative **9** over 4-nitrophthalonitrile in basic media afforded phthalonitrile derivative **8**. The substitution of morpholine rings by acetoxy groups led the precursor bis(acetoxy)phthalonitrile **7**. Cross condensation of **7** with 4-tert-butylphthalonitrile in the presence of Zn(AcO)₂ followed by methanolysis, turned out bis(hidroxymethyl)phthalocyanine **6**. In a last step, both primary alcohols were oxidized into formyl groups by means of periodinane IBX[13] affording phthalocyanine **3** in 9% overall yield (6 steps).

Polymerization of co-monomers **3** and **4** via Knoevenagel route into **1** was accomplished following a slightly modified procedure

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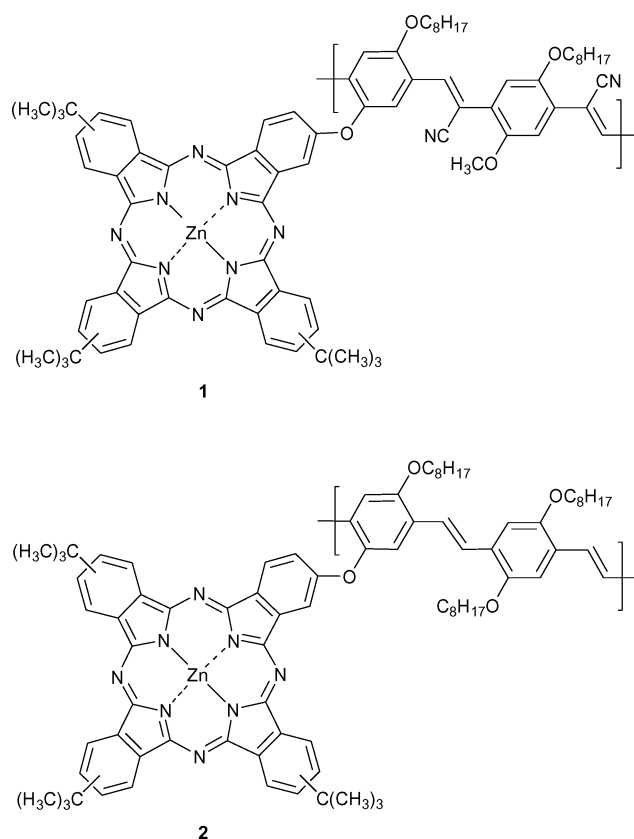
Fig. 1 Structures of oligomers **1** and **2**.

Table 1 GPC results for **1** and **2**, and size estimated based on M_n data

Derivative	M_w	M_n	PDI	Size based on M_n (repeating units)
1	8495	5730	1.5	*ca.* 4
2	7211	5132	1.4	*ca.* 3

located between 9.8 and 6.4 ppm. Around 4.6–3.6 ppm appeared the methylene and methoxy signals.

GPC results for compounds **1** and **2** as well as size estimate based on M_n data are depicted in Table 1. In order to have an idea about the size of the oligomeric materials it is important to remark that each repetitive unit is formed by two phenylenvinylene units.

Finally, the thermal stabilities of compounds **1** and **2** were tested by using the thermogravimetric analysis (TGA) under an inert atmosphere. Thermal degradation occurred in two steps with different weight loss ratio; the first one could be associated with the degradation of *tert*-butyl groups of phthalocyanine unit and PPV chain. The second one, at higher temperature, could be associated with the degradation of the phthalocyanine ring. It was noted also that compound **2** posses stability more similar to PPV and oPPV derivatives.[16]

Steady-state absorption spectroscopy of **1** and **2** reveals the known features of ZnPc. In particular, these are strong Soret bands around 350 nm, which are followed by Q bands around 680 nm. In addition, a broad absorbance is seen around 440 nm, which is ascribed to the PPV backbone. In comparison to a ZnPc reference the ZnPc's Soret bands in oligomers **1** and **2** are blue shifted up to 5 nm, while the Q bands give rise to 1–2 nm red shift. A summary of the absorption spectra is gathered in Fig. 2.

Fig. 2 Absorption spectra of ~6×10^{-6} M ZnPc (black spectrum), **1** (grey spectrum), and **2** (green spectrum) in THF at room temperature.

than that reported in a related case by Moratti and Holmes.[14] In our case, prolonged reaction times were necessary for obtaining the desired oligomers. The use of higher temperatures or amount of base (particularly Bu$_4$NOH), resulted in the occurrence of Pc degradation and hydrolysis of nitrile groups into carboxylic acids, thus decreasing the yield and the solubility of the oligomers. On the other hand, the synthesis of oligomeric derivative **2** was carried out by using the Wadsworth–Horner–Emmons reaction between derivatives **3** and **5**, in a similar fashion than that developed by Höhrold and co-workers[15] for simpler starting monomers. In our case, the reaction conditions afforded smaller oligomers than in the case of the Knoevenagel route mentioned above, nevertheless, higher amounts of base as well as higher temperatures or elongated reaction times do not give rise apparently neither Pc degradation nor oPPV cleavage.

Compounds **1** and **2** are well soluble in polar solvents such as THF or DMF, which makes easier the purification and characterization in solution, especially for **2** that posses a longer side alkoxy chain per repetitive unit. Both derivatives were characterized by techniques in solution and in the solid-state. FT-IR showed *trans*-configuration for the vinylenes in the case of **2** (δ_{oop} at 976 cm^{-1}). Likewise, bands due to formyl groups in terminal positions of the oligomeric chains were observed (1713 and 1695 cm^{-1} for **1** and **2**, respectively). **1** also showed a characteristic peak around 2216 cm^{-1} from nitrile groups. ^{1}H NMR spectroscopy showed broad signals due to isomers from both Pc and the conjugated backbone at similar shifts in both cases. At upper shift than 10.0 ppm appeared the signal from the terminal formyl groups. The aromatic signals from Pc and PPV backbone as well as the vinylene signals were

As a complement to the absorption spectra the fluorescence spectra of the ZnPc chromophores were measured in the ZnPc reference, **1** and **2**. The spectra—not shown—reveal a trend that essentially resembles that seen for the ground state spectra, namely, a red-shift. The fluorescence quantum yields, which were determined with respect to zinc 2,9,16,23-tetra-*tert*-butyl-29H,31H-phthalocyanine by the gradient method, are 0.3 (ZnPc reference), 0.23 (**2**) and 0.18 (**1**). The underlying trend of diminishing quantum yields is also reflected in time resolved measurements. The fluorescence lifetimes are 4.1 ns (ZnPc reference), 3.6 ns (**2**) and 3.3 ns (**1**). We believe that environmental differences are mainly responsible for the lower fluorescence quantum yields/faster fluorescence deactivation. Energy transfer and/or electron transfer are, however, unlikely to occur.
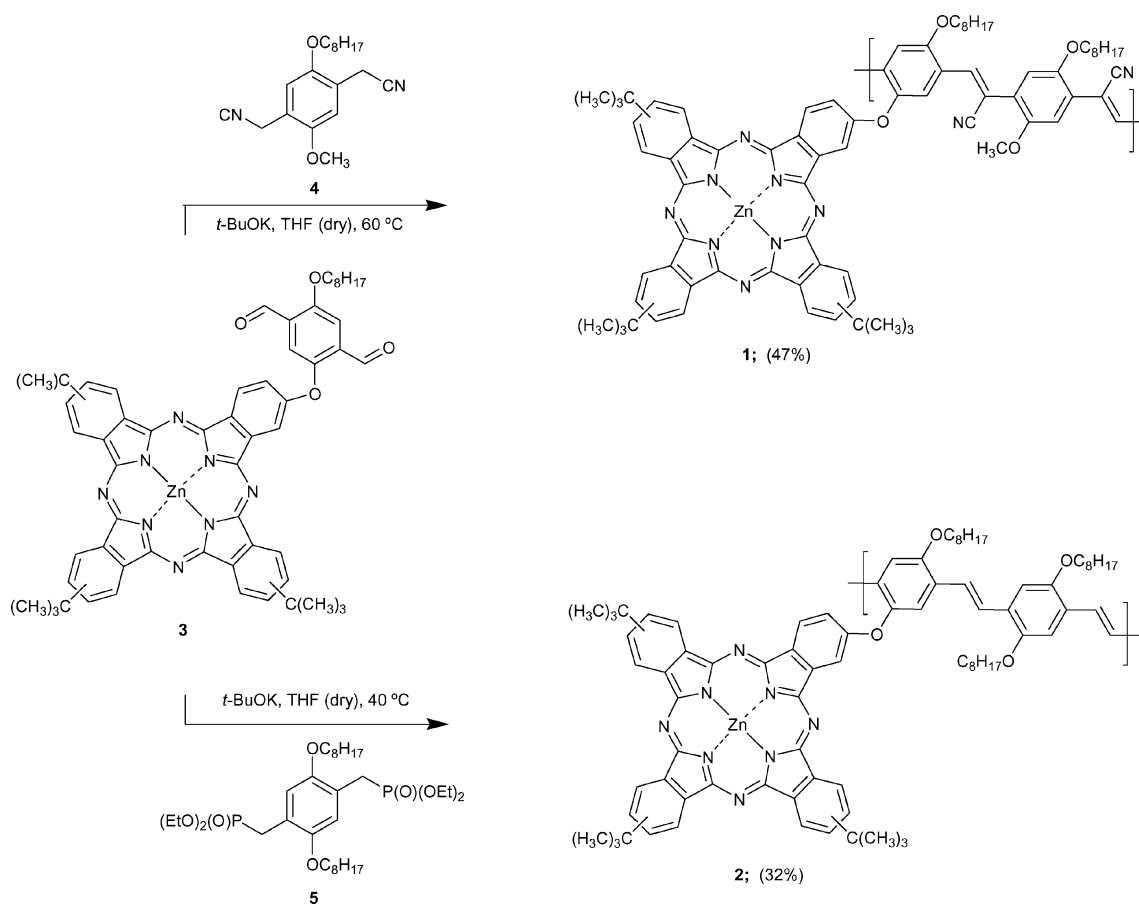
Scheme 1 Preparation of oligomers **1** and **2**.
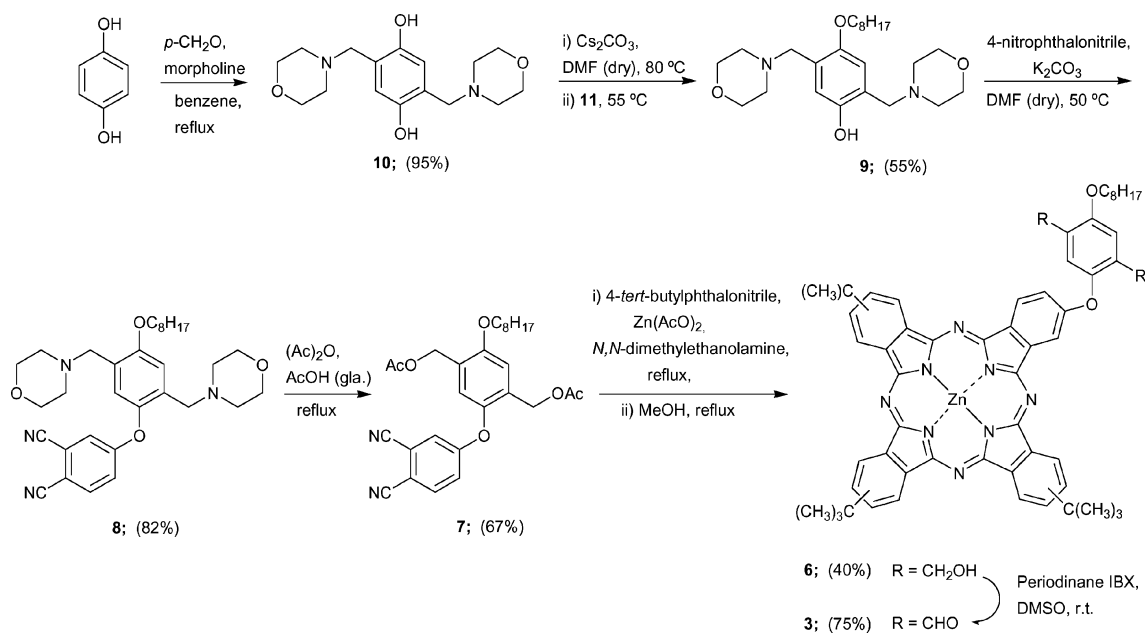
Scheme 2 Synthesis of phthalocyanine **3**.

For a better comparison of the different fluorescence properties 3-dimensional excitation (*i.e.*, 250–500 nm)/emission (*i.e.*, 600–850 nm) spectra—see Fig. 3. To subtract the excitation lamp spectra, we have plotted the quotient between the actual signal and the reference beam. In principle, the spectra are in excellent agreement with the aforementioned description. Excitation, for example, at 350 nm leads in ZnPc to fluorescence maxima at 688 nm. **1** and **2** show, however, maxima at 683 and 689 nm, respectively. Most important is the finding that we observe appreciable ZnPc fluorescence when exciting in the 425 and 500 nm region—a range without any significant ZnPc ground state absorption. Overall, this points to a photosensitization of the ZnPc unit when exciting the PPV units. The latter is nearly quantitative.
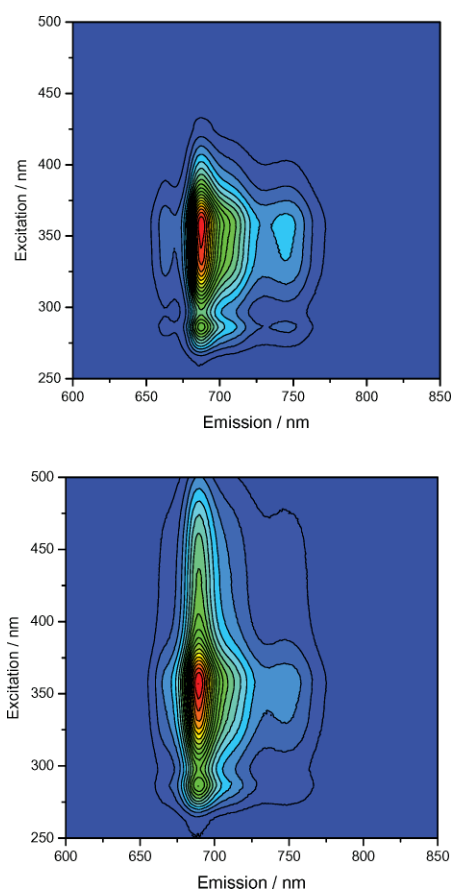

Fig. 4 Spectroelectrochemical oxidation of **1** in THF at variable potentials ranging from 0.0 V (black spectrum) to +0.7 V (dark blue spectrum).

Fig. 3 3D excitation-fluorescence spectra of ZnPc (~6 × 10⁻⁶ M)—upper part and **2**—lower part in THF at room temperature.

In the next of our investigation, we conducted electrochemistry and spectroelectrochemistry to confirm the redox activity of ZnPc in the reference and linked to the oligomer backbone and the signature of the oxidized species, which becomes ultimately important in the context of photoinduced electron transfer processes. Electrochemical experiments in THF revealed oxidation potentials for **1** at +0.72 V and for **2** at +0.61 V *vs.* Ag wire, respectively. We see—in line with our expectations—the radical cation signature of ZnPc all throughout the samples at around 840 nm; see, for example, Fig. 4. In particular, the one-electron oxidized form of ZnPc shows significant spectroscopic changes in the differential absorption spectra, *i.e.* maxima and bleaching (b) at 350 (b), 424, 518, 608 (b), 725 and 838 nm. For **1** the features develop at 350
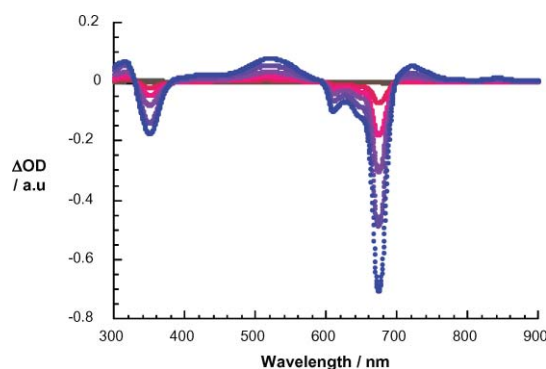
(b), 520, 609 (b), 719 and 842 nm, while the corresponding values are 350 (b), 380, 532, 609 (b), 718 and 842 nm for **2**.

In the last step of our investigations we tested the singlet–singlet and triplet–triplet features of the ZnPc, **1** and **2** and their excited state interactions by means of transient absorption measurements. An illustration is given in Fig. 5, which gathers the differential absorption changes with time delays between 1.5 and 3000 ps. To be precise, photoexcitation at 660 nm leads to the nearly instantaneous formation of the ZnPc singlet excited state, for which the following features were noted: maxima at 485 and 805 nm and minima at 605 and 680 nm. No significant differences were, however, noted for the ZnPc reference and the two oligomers (*i.e.*, **1** and **2**). The singlet excited state is metastable and starts to decay slowly on the femtosecond/picosecond time scale. When turning to the time profiles at 800 nm—see Fig. 5—a common process is seen in all samples at short times (*i.e.*, up 1.5 ps). This ultra fast process reflects the formation of the singlet excited state as it rapidly evolves from a higher lying excited state.

In the ZnPc reference all that is seen afterwards is the slow intersystem crossing to the triplet manifold. The main spectral feature of the latter is a broad transient with a notable maximum at 500 nm and with two minima at 350 and 680 nm. In the absence of molecular oxygen, the ZnPc triplet excited state returns to the singlet ground state over the course of several microseconds. Back to the intersystem crossing, the underlying kinetics in the ZnPc reference are strictly mono-exponential and resemble those measured in the fluorescence experiments with a value of approximately 4 ns. This is different in the PPV containing **2**. Now, the time-absorption profiles are best fitted by a double exponential fit with values of 150 ps and ~2.5 ns.

The efficiency by which the ZnPc triplet excited state was formed was probed by singlet oxygen formation. The ground state of molecular oxygen—a triplet—is known to interact with triplet excited states—including that of ZnPc—*via* diffusion controlled processes to yield quantitatively singlet oxygen. A fingerprint of the latter is its distinct emission at 1265 nm, see Fig. 6. In this context, we have compared the singlet oxygen quantum yields by photoexciting the ZnPc reference, **1**, **2** with equal absorbance at the 620 nm excitation wavelength. Relative to ZnPc, the quantum yields in **1** and **2** were reduced by 23% in both cases.

The lower singlet oxygen quantum yields track the lower ZnPc fluorescence quantum yields and, in turn, identify environmental effects for the latter as the overall bottle neck.
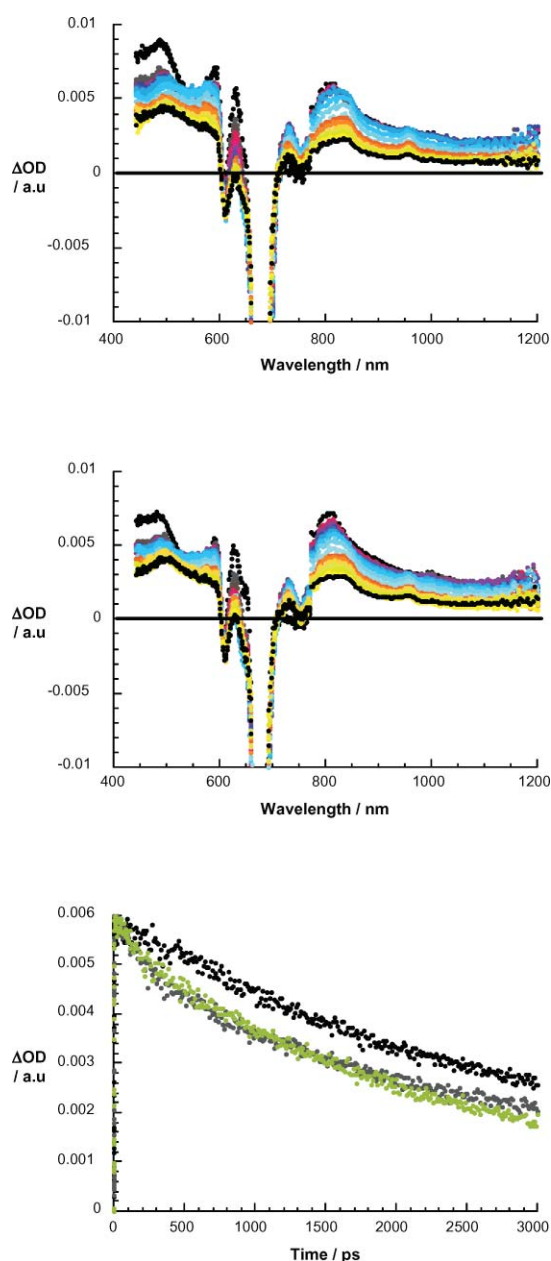
Fig. 5 Upper part, differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (660 nm) of ZnPc (~3 × 10⁻⁵ M) with several time delays between 0 and 3000 ps at room temperature. Central part, differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (660 nm) of **1** (~3 × 10⁻⁵ M) with several time delays between 0–3000 ps at room temperature. Lower part, time-absorption profiles of the femtosecond spectra at 810 nm, monitoring the intersystem crossing in THF–ZnPc (black spectrum), **1** (grey spectrum) and **2** (green spectrum).

Experimental

General

Chemicals were purchased from Aldrich Chemical Co. and used as received without further purification. IR spectra were recorded with a Bruker Vector 22 spectrophotometer. EI-MS spectra were determined on a VG AutoSpec instrument, MALDI-TOF MS and HRMS spectra were recorded with a Bruker Reflex III
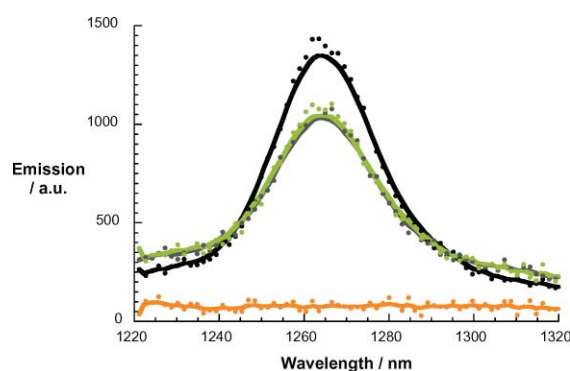

Fig. 6 Singlet oxygen phosphorescence of ZnPc (black spectrum), **1** (grey spectrum), **2** (green spectrum) and THF (orange spectrum) in oxygen saturated THF at room temperature with samples showing equal absorbance of 0.1 at the excitation wavelength of 620 nm.

spectrometer. NMR spectra were recorded with a Bruker AC-300 instrument. Column chromatography was carried out on silica gel Merck-60 (230–400 mesh, 60 Å) and TLC on aluminium sheets pre-coated with silica gel 60 F254 (E. Merck). M_w and M_n were determined by GPC with Perkin Elmer Series 200 pump, oven and UV-vis detector. The eluent was DMF containing 0.1% (w/v) LiBr. The wavelength was 271 nm, the oven temperature was 70 °C, and the flow was 1 mL min⁻¹. Polystyrene standards were used as references. TGA were carried out on a TA Q500 analyzer using 5 mg samples under a nitrogen atmosphere using a high-resolution dynamic method. Steady state absorption spectra were measured by a Cary5000 (Varian) two beam spectrometer. Emission spectra were recorded by using a FluoroMax-3 (HORIBA Jobin Yvon). The experiments were performed at room temperature. Time correlated single photon counting (TCSPC) spectra were taken with a Fluorolog system (HORIBA Jobin Yvon). The sample was excited by a NanoLED-605 (peak wavelength 611 nm) and the signal was detected by a Hamamatsu MCP photomultiplier (type R3809U-50). The time profiles were recorded at 680 nm. Singlet oxygen phosphorescence spectra were measured by a Fluorolog spectrometer (HORIBA Jobin Yvon), too. Here, the optical detection was performed by a Symphony InGaAs array in combination with an iHR320 imaging spectrometer. Femtosecond transient absorption studies were performed with 660 nm laser pulses (1 kHz, 150 fs pulse width, ~100 nJ) from an amplified Ti : sapphire laser system (Clark-MXR, Inc.). All electrochemical experiments were performed in deaerted THF solutions containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) at 298 K. Cyclic voltammetry measurements were carried out on an EG&G Princeton Applied Research potentiostat (Model 263A). A three-electrode system was used and consisted of a glassy carbon working electrode (d = 2 mm), a platinum wire counter electrode, and silver wire as quasi-reference electrode. Ferrocene was used as an internal standard. Spectroelectrochemical experiments were performed with a home made setup containing a potentiostat (HEKA elektroniks, type PG 284) and a Lambda2 UV-VIS spectrometer (Perkin Elmer). The working electrode has been a platinum gauze (99.9%, 1024 mesh/cm², 0.06 mm wire diameter) from ChemPur®. A platinum plate (8 mm × 5 mm) and a silver wire have been used as a counter electrode and a quasi-reference electrode, respectively.

Synthesis of phthalocyanine precursor 3

(2-Ethyl)hexyl-4-methylbenzenesulfonate (11). To a solution of 2-ethylhexanol (5.00 g, 34.70 mmol) in dry $CHCl_3$ (37 cm³) cooled at 0 °C was added pyridine (5.7 cm³, 69.40 mmol) under argon atmosphere at once. Then, 4-methylbenzenesulfonyl chloride (9.90 g, 52.0 mmol) was added in a few portions while keeping the temperature below 10 °C. The mixture was stirred at low temperature for 3 h, and then portioned with water and diethyl ether (125 cm³ each). The organic layer was washed with solutions of hydrochloric acid (1.0 M, 4 × 50 cm³), sodium bicarbonate (2 × 60 cm³) and finally with brine (2 × 60 cm³). The organic extracts were dried over magnesium sulfate, filtered and the solvent evaporated under reduced pressure to afford **11** (10.24 g, 99%) as a colourless oil; δ_H (300 MHz; $CDCl_3$; Me_4Si) 0.78 (3 H, t, J 7.6, CH_3), 0.82 (3 H, t, J 6.9, CH_3), 1.0–1.40 (8 H, m, $(CH_2)_4$), 1.52 (1 H, st, J 6.1, $ArOCH_2CH$), 2.43 (3 H, s, $ArCH_3$), 3.91 (2 H, s, J 5.3, $ArOCH_2$), 7.33 (2 H, d, J 8.6, H-3, H-5) and 7.78 (2 H, d, J 8.6, H-2, H-6); δ_C (75 MHz; $CDCl_3$; Me_4Si) 10.7 (CH_3), 13.9 (CH_2), 21.5 (CH_2), 22.8 ($ArCH_3$), 23.2 (CH_2), 28.6 (CH_2), 29.8 (CH_2), 39.0 ($ArOCH_2CH$), 72.5 ($ArOCH_2$), 127.8 (C-2, C-6), 129.7 (C-5, C-3), 133.1 (C-1) and 144.6 (C-4); m/z (EI) 284 (M^+, 1%), 173 (M_2 [$M - C_8H_{17}$]⁺, 39%), 155 (M_3 [$M - OC_8H_{17}$]⁺, 64%), 112 (M_4 [C_8H_{17}]⁺, 93%) and 91 (M_5 [C_7H_7]⁺, 100%).

2,5-Bis(N-methylmorpholino)-1,4-dihydroquinone (10). A mixture of 1,4-dihydroquinone (15.0 g, 0.136 mol), p-formaldehyde (12.26 g, 0.449 mol) and morpholine (35.6 g, 0.409 mol) in benzene (375 cm³) was refluxed in a Dean–Stark equipped set for 18 h. After cooling, the white precipitated formed was filtered off, washed with cold benzene (50 cm³) and dried in vacuum. The solid was purified by recrystallization from acetone, obtaining **10** (39.84 g, 95%) in the form of non-coloured crystals. mp 193 °C; δ_H (300 MHz; DMSO-d_6; Me_4Si) 2.39 (4 H, bt, J 4.1, $N(CH_2)_2(CH_2)_2O$), 3.47 (4 H, s, $ArCH_2N$), 3.57 (8 H, bt, J 4.5, $N(CH_2)_2(CH_2)_2O$), 6.53 (2 H, s, H-3, H-6) and 9.37 (2 H, bs, ArOH); δ_C (75 MHz; DMSO-d_6; Me_4Si) 53.3 ($ArCH_2N$), 59.0 ($N(CH_2)_2(CH_2)_2O$), 66.7 ($N(CH_2)_2(CH_2)_2O$), 116.5 (C-3, C-6), 122.0 (C-2, C-5) and 149.2 (C-1, C-4); m/z (EI) 308 (M^+, 18%), 221 (M_1 [$M - C_4H_8NO$]⁺, 100%), 136 (M_2 [$M_1 - C_4H_8NO$]⁺, 12%), 100 (M_3 [$C_5H_{10}NO$]⁺, 11%) and 86 (M_4 [C_4H_8NO]⁺, 38%).

2,5-Bis(N-methylmorpholino)-4-(2-ethyl)hexyloxyphenol (9). A mixture of **10** (3.37 g, 10.93 mmol) and Cs_2CO_3 (1.8 g, 5.48 mmol) in dry DMF (50 cm³) was heated at 80 °C under argon atmosphere for 2 h. Subsequently, a solution of **11** (1.56 g, 5.48 mmol) in dry DMF (5 cm³) was added dropwise. Then, the reaction was brought to 55 °C and stirred for 72 h. After cooling at room temperature, the mixture was poured into 400 cm³ of brine and extracted exhaustively with diethyl ether (12 × 50 cm³). The organic extract was washed with water and brine (50 cm³ each), dried over Na_2SO_4 and the solvent eliminated in vacuum. The pure compound was isolated from the brown oily residue on a column chromatography on silica using hexane–tetrahydrofuran (1 : 1 v/v) as eluent. In this way, compound **9** (1.26 g, 55%) was obtained as a pale yellow oil that solidified by standing. mp 60–62 °C; δ_H (300 MHz; DMSO-d_6; Me_4Si) 0.88 (3 H, t, J 4.5, CH_3), 0.92 (3 H, t, J 7.5, CH_3), 1.20–1.55 (8 H, m, $(CH_2)_4$), 1.68 (1 H, st, J 8.9, $ArOCH_2CH$), 2.50 (8 H, m, $N(CH_2)_2(CH_2)_2O$), 3.48 (2 H, s, $ArCH_2N$), 3.65 (2 H, s, $ArCH_2N$), 3.69 (2 H, d,

J 6.4, $ArOCH_2$), 3.73 (8 H, m, $N(CH_2)_2(CH_2)_2O$), 6.49 (1 H, s, H-6), 6.84 (1 H, s, H-3) and 9.95 (1 H, bs, ArOH); δ_C (75 MHz; $CDCl_3$; Me_4Si) 11.2 (CH_3), 14.0 (CH_3), 23.1 (CH_2), 24.1 (CH_2), 29.1 (CH_2), 30.7 (CH_2), 39.7 ($ArOCH_2CH$), 53.0 ($ArCH_2N$), 53.6 ($ArCH_2N$), 61.6 ($N(CH_2)_2(CH_2)_2O$), 61.9 ($N(CH_2)_2(CH_2)_2O$), 66.8 ($N(CH_2)_2(CH_2)_2O$), 67.1 ($N(CH_2)_2(CH_2)_2O$), 71.2 ($ArOCH_2$), 112.5 (C-3), 118.1 (C-6), 119.3 (C-5), 126.9 (C-2) and 150.7 (C-1, C-4); m/z (EI) 420 (M^+, 62%), 335 (M_1 [$M − C_4H_8NO$]⁺, 26%), 248 (M_2 [$M_1 − C_4H_8NO$]⁺, 45%), 221 (M_3 [$M_2 − (C_4H_8NO)$]⁺, 95%), 136 (M_6 [($M_2 − C_4H_8NO$)⁺], 97%), 100 (M_7 [($C_5H_{10}NO)^+$], 29%), 86 (M_8 [($C_4H_8NO)^+$], 88%).

4[(4-(2-Ethyl)hexyloxy-2,5-bis(N-methylmorpholino)]phenoxy-phthalonitrile (8). 4-Nitrophthalonitrile (1.29 g, 7.45 mmol), K_2CO_3 (3.6 g, 25.85 mmol) and **9** (3.10 g, 7.37 mmol) in dry DMF (125 cm³) were heated at 50 °C under argon atmosphere for 36 h. After cooling to room temperature, the mixture was poured into 500 cm³ of brine and extracted with diethyl ether (4 × 50 cm³). The organic extracts were joined, washed with solutions of sodium hydroxide (0.1 M, 3 × 50 cm³), sodium bicarbonate (2 × 50 cm³) and brine (2 × 50 cm³) and dried over magnesium sulfate. After filtration, the solvent was evaporated giving an oily mixture that solidified. The crude was purified by column chromatography on silica using ethyl acetate as eluent, affording **8** (3.30 g, 82%) as a yellow oil that solidified by standing. ν_{max}(KBr pellets)/cm⁻¹: 2930, 2862, 2808, 2235 ν_{st}(C≡N), 1497, 1456, 1416, 1389, 1362, 1321, 1254, 1200, 1119, 1038 ν_s(C–O–C), 1011 and 866 ν_{as}(C–O–C); δ_H (300 MHz; $CDCl_3$; Me_4Si) 0.93 (3 H, t, J 7.0, CH_3), 0.97 (3 H, t, J 6.4, CH_3), 1.23–1.67 (8 H, m, $(CH_2)_4$), 1.76 (1 H, sp, J 5.9, $ArOCH_2CH$), 2.36 (4 H, bt, $N(CH_2)_2(CH_2)_2O$), 2.47 (4 H, bt, $N(CH_2)_2(CH_2)_2O$), 3.32 (2 H, s, $ArCH_2N$), 3.51 (4 H, bt, $N(CH_2)_2(CH_2)_2O$), 3.52 (2 H, s, $ArCH_2N$), 3.68 (4 H, bt, $N(CH_2)_2(CH_2)_2O$), 3.89 (2 H, d, J 5.3, $ArOCH_2$), 6.95 (1 H, s, H-3′), 7.05 (1 H, s, H-6′), 7.12 (1 H, d, $J_{m,3-5}$ 2.5, H-3), 7.16 (1 H, dd, $J_{o,5-6}$ 8.6 and $J_{m,3-5}$ 2.5, H-5) and 7.69 (1 H, d, $J_{o,5-6}$ 8.6, H-6); δ_C (75 MHz; $CDCl_3$; Me_4Si) 10.3 (CH_3), 13.2 (CH_3), 22.0 (CH_2), 23.1 (CH_2), 28.2 (CH_2), 29.7 (CH_2), 38.6 ($ArOCH_2CH$), 52.4 ($N(CH_2)_2(CH_2)_2O$), 52.7 ($N(CH_2)_2(CH_2)_2O$), 55.0 ($ArCH_2N$), 56.3 ($ArCH_2N$), 65.8 ($N(CH_2)_2(CH_2)_2O$), 66.0 ($N(CH_2)_2(CH_2)_2O$), 69.8 ($ArOCH_2$), 107.0 (C-1), 112.8 (C-3′), 114.1 (CN), 114.5 (CN), 116.4 (C-2), 119.4 (C-6′), 119.5 (C-5′), 121.9 (C-3), 127.0 (C-5), 128.7 (C-2′), 134.1 (C-6), 143.6 (C-1′), 154.5 (C-4′) and 161.9 (C-4); m/z (EI) 546, 460 (M_2 [$M − C_4H_8NO$]⁺, 21%), 447 (M_3 [$M_2 − C_5H_{10}NO$]⁺, 85%), 349 (M_4 [$M_2H − C_8H_{17}$]⁺, 45%), 262 (M_5 [$M_4H − C_4H_8NO$]⁺, 26%) and 86 (M_6 C_4H_8NO]⁺, 100%).

4[(4-(2-Ethyl)hexyloxy-2,5-bis(methylacetoxy)]phenoxyphthalo-nitrile (7). Derivative **8** (3.4 g, 6.20 mmol) was reacted in a mixture of acetic anhydride (70 cm³) and glacial acetic acid (15 cm³) under argon atmosphere for 4 d. When consumption of **8** was complete, the solvents were evaporated and the residue dissolved in chloroform and washed with water (100 cm³ each). The organic extract was further washed with a solution of hydrochloric acid (0.1 M, 3 × 60 cm³), neutralised with a saturated sodium bicarbonate solution (2 × 50 cm³), brine (2 × 50 cm³) and dried over magnesium sulfate. 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 hexane–ethyl acetate (2 : 1 v/v) as

eluent to give **7** (2,04 g, 67%) as a pale yellow oil that solidified by standing. mp 71–73 °C; ν_{max}(KBr pellets)/cm^{-1}: 2962, 2934, 2864, 2235 ν_{st}(C≡N), 1742 ν_{st}(C=O), 1605, 1497, 1456, 1416, 1389, 1319, 1229 ν_{as}(C–O), 1196, 1059 ν_s(C–O), 881, 854, 773, 733, 613, 525 and 457; δ_H (200 MHz; CDCl$_3$; Me$_4$Si) 0.88–0.99 (6 H, m, (CH$_3$), 1.23–1.65 (8 H, m, (CH$_2$)$_4$), 1.76 (1 H, st, J 5.9, ArOCH$_2$C*H*), 3.93 (2 H, d, J 5.4, ArOC*H*$_2$), 5.0 (2 H, s, ArC*H*$_2$OC(O)CH$_3$), 5.13 (2 H, s, ArC*H*$_2$OC(O)CH$_3$), 6.99 (1 H, s, H-3′), 7.00 (1 H, s, H-6′), 7.20 (1 H, dd, $J_{o,5-6}$ 8.6 and $J_{m,3-5}$ 2.5, H-5), 7.23 (1 H, d, $J_{m,3-5}$ 8.6, H-3) and 7.72 (1 H, d, $J_{o,5-6}$ 8.6, H-6); δ_C (75 MHz; CDCl$_3$; Me$_4$Si) 11.2 (CH$_3$), 14.0 (CH$_3$), 20.6 (ArCH$_2$OC(O)*C*H$_3$), 22.9 (CH$_2$), 23.9 (CH$_2$), 29.0 (CH$_2$), 30.5 (CH$_2$), 39.4 (ArOCH$_2$*C*H), 60.9 (ArCH$_2$OC(O)*C*H$_3$), 70.9 (ArOCH$_2$), 108.7 (C-1), 113.2 (C-3′), 114.9 (CN), 115.3 (CN), 117.5 (C-6′), 120.7 (C-2), 120.8 (C-3), 121.9 (C-5), 127.2 (C-5′), 129.0 (C-2′), 135.3 (C-6), 144.1 (C-1′), 155.0 (C-4′), 162.2 (C-4), 170.2 (Ar*C*(O)OCH$_3$) and 170.5 (Ar*C*(O)OCH$_3$); m/z (EI) 492 (M$^+$, 25%), 380 (M$_1$ [MH – C$_8$H$_{17}$]$^+$, 6%), 320 (M$_2$ [(M$_1$ – C$_2$H$_3$O$_2$)$^+$, 100%) and 260 (M$_3$ [M$_2$ – C$_2$H$_3$O$_2$]$^+$, 13%).

9,16,23-Tri-*tert*-butyl-2-[4-(2-ethyl)hexyloxy-2,5-bis(hydroxymethyl)]phenoxyphthalocyaninatozinc(II) (regio-isomer mixture) (6). Phthalonitrile **7** (600 mg, 1.22 mmol), 4-*tert*-butyphthalonitrile (900 mg, 4.88 mmol) and Zn(AcO)$_2$ (293 mg, 1.60 mmol) were stirred in DMAE (10 cm^3) and refluxed under argon atmosphere for 20 h. Then, the solution was cooled down and methanol (30 cm^3) was added. The mixture was refluxed again for further 2 h, and after cooling, poured into water (100 cm^3). 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 cm^3 each), and methanol (50 cm^3). Afterwards, the solid was dried and redissolved in tetrahydrofuran and purified by column chromatography (SiO$_2$) using hexane–dioxane (2 : 1 v/v) as eluent. The isolated blue solid obtained was triturated in hot hexane, filtered and dried to afford phthalocyanine **6** (501 mg, 40%) as a dark blue solid. mp > 250 °C; (found: C 70.0, H 6.3, N 11.0. C$_{60}$H$_{64}$N$_8$O$_4$Zn requires C 70.2, H 6.3, N 10.9%); λ_{max}(tetrahydrofuran)/nm (log ε) 349 (4.5), 612 (4.2) and 679 (4.9); δ_H (500 MHz; CDCl$_3$; Me$_4$Si) 0.5–2.0 (42 H, m, CH, CH$_2$, CH$_3$), 4.2 (2 H, d, ArOCH$_2$), 5.0–5.7 (6 H, m, ArOC*H*$_2$O*H*), 6.8–7.0 (2 H, m, ArH), 7.8–8.2 (4 H, m, Pc–H) and 8,8–9.4 (8 H, m, Pc–H); m/z (MALDI, dithranol) 1030–1024 (C$_{60}$H$_{64}$N$_8$O$_4$Zn requires 1026.59).

9,16,23-Tri-*tert*-butyl-2-[4-(2-ethyl)hexyloxy-2,5-diformyl] phenoxyphthalocyaninatozinc(II) (regio-isomers mixture) (3). To a well stirred and colourless solution of periodinane 1-hydroxy-1,2-benziodoxole-3(1*H*)-one-1-oxide (IBX) (112 mg, 0.312 mmol) in dimethyl sulfoxide (47 cm^3), compound **6** (128 mg, 0.097 mmol) was added at once. The solution was stirred at room temperature for 5 h and then, poured over brine (200 cm^3) and extracted with diethyl ether (3 × 40 cm^3). The organic layer was separated, washed with a saturated solution of sodium bicarbonate (2 × 60 cm^3), brine (2 × 60 cm^3) and dried over sodium sulfate. After filtration of the drier agent, the solvent was evaporated and the blue solid was purified by column chromatography on silica gel using hexane–dioxane (3 : 1 v/v) as eluent, affording aldehyde **3** as dark blue solid (95 mg, 75%). mp > 250 °C; (found: C 70.0, H 6.0, N 10.5. C$_{60}$H$_{60}$N$_8$O$_4$Zn requires C 70.5, H 5.9, N 10.9%); λ_{max}(chloroform)/nm (log ε) 350 (4.8), 608 (4.4) and 674 (5.1);

ν_{max}(KBR pellets)/cm^{-1}: 2966, 2926, 2872, 1720 ν_{st}(C=O), 1693, 1612, 1497, 1429, 1402, 1335, 1267, 1213, 1159, 1092, 1051, 984, 930, 835, 754, 700, 673, 525 and 449; δ_H (500 MHz; CDCl$_3$; Me$_4$Si) 0.9–2.1 (42 H, m, CH, CH$_2$, CH$_3$), 4.17 (2 H, bs, ArOCH$_2$), 7.5–8.3 (6 H, m, Pc–H, ArH), 8.6–9.3 (8 H, m, Pc–H), 10.52 (1 H, m, CHO) and 10.86 (1 H, m, CHO); m/z (MALDI, dithranol) 1027–1020 (C$_{60}$H$_{60}$N$_8$O$_4$Zn requires 1022.56).

Synthesis of oPPV–Pc oligomers

Synthesis of oPPV 1 *via* Knoevenagel reaction. Diformyl derivative **3** (50 mg, 0.049 mmol), 2,5-bis(cyanomethyl)-4-(2-ethyl)hexyloxy-anisol (**4**) (16 mg, 0.051 mmol) and anhydrous potassium *tert*-butoxide (9 mg, 0.08 mmol) were dissolved in a mixture of dry tetrahydrofuran (6.0 cm^3) and dry *tert*-butanol (1.0 cm^3). The solution was heated at 60 °C and then a solution of tetrabutylammonium hydroxide (15 µL, 0.1 M in methanol) was added at once, what turned the solution into dark green colour. After heating for 24 h, further anhydrous potassium *tert*-butoxide (9 mg, 0.08 mmol) and tetrabutylammonium hydroxide solution (15 µL, 0.1 M in methanol) were added maintaining the temperature until consumption of starting diformyl compound (24 h) precipitating an abundant dark green solid. Then, the solvents were evaporated and the residue was triturated in methanol (30 cm^3) acidified with a drop of acetic acid in an ultrasound bath. The solid obtained was filtered off and washed with plenty of hot methanol until the washing solvent was clear. The oligomeric material was redissolved in the minimum amount of tetrahydrofuran and re-precipitated with methanol. The precipitated was filtered off and washed with 50 cm^3 of mixtures hexane–acetone (3 : 1) and hexane–chloroform (3 : 1), and finally with hexane. Further purification can be accomplished on a Biobeads® column, with tetrahydrofuran as solvent. The main fraction (first to elute) was separated and the solvent eliminated. After washing with a mixture of hexane–acetone (1 : 1) the green compound was dried in vacuum affording **1** (30 mg, 47%) as a green solid. λ_{max}(tetrahydrofuran)/nm: 352, 441 (h), 610 and 680; ν_{max}(KBr pellets)/cm^{-1}: 2964, 2937, 2870, 2216 ν_{st}(C≡N), 1713 ν_{st}(C=O), 1618, 1497, 1470, 1416, 1335, 1267, 1213, 1196, 1092, 1051, 835, 754 and 700; δ_H (500 MHz; THF-d$_8$; Me$_4$Si) 0.6–2.3 (m, CH, CH$_2$, CH$_3$, C(CH$_3$)$_3$), 3.8–4.6 (m, ArOCH$_2$, ArOCH$_3$), 6.7–7.5 (brs, ArH), 7.5–8.2 (brs, ArH), 8.2–8.5 (m, Pc–H), 9.3–9.8 (m, Pc–H); m/z (MALDI, dithranol) 2926, 2625–2614 (dimer), 2625–2656, 2355–2402, 1912–1905, 1688–1680, 1667–1657, 1654–1646, 1645–1636, 1629–1620, 1613–1605, 1380–1370, 1342–1330, 1329–1320 (monomer); SEC (DMF, PS standards): M_w = 8495; M_n = 5730; PD = 1.5; TGA (°C/mass lost): 352/−30%, 473/−7%.

Synthesis of oPPV 2 *via* Wadsworth–Horner–Emmons reaction. Diformyl derivative **3** (40 mg, 0.039 mmol) and 2,5-di-*n*-octyloxy-1,4-xylene-bis(diethylphosphonate)ester (**5**) (26 mg, 0.041 mmol) were dissolved in dry tetrahydrofuran (6.0 cm^3) under argon atmosphere. Then, potassium *tert*-butoxide (9 mg, 0.08 mmol) suspended in dry tetrahydrofuran (4.0 cm^3) was added drop by drop under stirring. The solution was heated at 40 °C for 12 h and then potassium *tert*-butoxide (9 mg, 0.08 mmol) was added. The solution was heated for further 12 h until consumption of diformyl precursor, precipitating an abundant dark green solid. Tetrahydrofuran was eliminated under reduced pressure and the residue triturated in methanol (30 cm^3) acidified with a drop of

acetic acid in an ultrasound bath. The suspension was filtered off and washed with plenty of hot methanol until the washing solvent was clear. The oligomeric material was purified from remaining shorter oligomers on a SEC column (Biobeads®) in tetrahydrofuran. The solvent was removed in vacuum and the green material washed with hot acetone and dried in vacuum to afford **2** (32 mg, 32%) in the form of a dark green solid. λ_{max}(tetrahydrofuran)/nm: 346, 441 (h), 614 and 680; ν_{max}(KBr pellets)/cm^{-1}: 2964, 2870, 1695 ν_{st}(C=O), 1614, 1489, 1394, 1340, 1286 ν_{st}(P=O), 1259, 1219, 1138, 1097 ν_{st}(C–O–C), 1057, 976 $\nu_{\delta\,oop}$ (C=C–H *trans*), 949, 922, 868, 841, 748, 694, 606, 534 and 449; δ_H(500 MHz; THF-d$_8$; Me$_4$Si) 0.5–2.3 (m, CH, CH$_2$, CH$_3$, C(CH$_3$)$_3$), 3.6–4.4 (m, ArOCH$_2$), 6.4–6.9 (brs, Ar–CH$_2$=CH$_2$–Ar′), 7.0–7.3 (brs, ArH), 8.2–8.5 (m, PcH) and 8.7–9.8 (m, PcH); *m/z* (MALDI, dithranol) 5553 (tetramer), 5240, 5076–5064, 4772–4760, 4208–4194 (trimer), 3903–3892, 3728–3713, 3605–3598, 3439–3428, 3425–3407, 3340–3328, 3216–3208, 3127–3115, 2859–2847 (dimer), 2379–2367, 1987–1981, 1866–1859, 1777–1768, 1527–1517, 1510–1501 (monomer), 1403–1394, 1386–1379; SEC (DMF, PS standards): $M_w = 7211$; $M_n = 5132$; PD = 1.4; TGA (°C/mass lost): 382/–49%, 477/–7%.

Conclusions

Diformylphthalocyanine **3** was a key monomer in the synthesis of two poly(*p*-phenylenevinylene) oligomers (oPPV) **1** and **2** laterally substituted by phthalocyanines (Pc). Knoevenagel and Wadsworth–Horner–Emmons reactions were employed for this purpose, respectively. The functionalised conjugated oligomers appears to be a viable way for the preparation of ambipolar conducting "double-cable" polymers (p–n type polymers) with potential applications in organic solar cells. Photophysical investigations—by means of fluorescence and transient absorption measurements—further corroborated the potential of our approach. In particular, all the features that the ZnPc reveals in a reference are principally preserved in **1** and **2**, despite the high ZnPc loading.

Acknowledgements

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