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Efficient electron transfer in β-substituted porphyrin-C_{60} dyads connected through a *p*-phenylenevinylene dimer

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ABSTRACT

Two new porphyrin-C_{60} dyads have been synthesized in which the electroactive moieties have been connected through a *p*-phenylenevinylene dimer. The electrochemical study confirms the amphoteric redox behavior of these dyads. Irradiation of these compounds gives rise to the corresponding radical pair confirming that substitution on the β-position of the porphyrin facilitates the electronic communication between the porphyrin and C_{60}.

1. Introduction

One of the central issues of molecular electronics is the study of molecular charge transport.[1] Donor-Bridge-Acceptor (DBA) systems constitute excellent model compounds to assess electron transfer over long distances.[2] In these systems, photo-induced electron transfer and irradiation can cause the transport of an electron from the donor to the acceptor. The rate of electron transport is governed by parameters related to the donor and acceptor properties, as the driving force (ΔG^0) and the reorganization energy (λ), and also by the electronic coupling (V), which is affected both by the structure of the bridge and the donor-bridge energy gap. The efficiency of electron transfer (eT) decreases exponentially with increasing molecular wire length according to the electron transfer rate constant, k_{ET},

$$k_{ET} = k_0 e^{-\beta R_{DA}}$$

where k_0 is a kinetic prefactor, R_{DA} represents the donor–acceptor distance, and β is the attenuation factor, which depends on the intrinsic electronic properties of the bridge. Typical values for β range between 1.0 and 1.4 Å^{-1} for proteins, and between 0.01 and 0.06 Å^{-1} for highly efficient π-conjugated bridges.[3]

A key aspect for achieving efficient molecular wire behavior in DBA systems is the effective matching of orbital energies between the donor and bridge components, and between the acceptor and bridge components.[4] Thus, the extraordinarily low β value (~0.01 Å^{-1}) determined for *ex*TTF-*o*PPV-C_{60} (**1**) systems can be best understood in terms of the effective π-conjugation between the donor, the oligo-PPV bridge and the C_{60} moiety.[5]

This β value is increased when either the donor moiety or the bridge are changed, probably due to a lower effective conjugation. β factors of 0.2 Å^{-1} or 0.09 Å^{-1} have been obtained for *ex*TTF-*o*PPE-C_{60} (**2**)[6] and *ex*TTF-oligofluorene-C_{60} (**3**)[7] systems, respectively. Also, in TPP-*o*PPV-C_{60} (**4**) systems, values of β=0.03 Å^{-1} were determined, which are larger than those found when *ex*TTF acts as the donor moiety, thus evidencing the lower *para* conjugation between the TPP donor unit and the π-conjugated oligomer.[8] This loss of conjugation has been accounted for the dihedral angles between the TPP phenyl ring and the first ring of the oligomer unit (~30°) and the deviation from planarity along the oligomer unit.

Schuster et al.[9] have studied the energy and electron transfer processes in alkynyl-linked porphyrin-C_{60} dyads and compared the photophysical behaviors of β-alkynylZnP-C_{60} (**5a**–**c**) and *para*-phenylalkynylZnP-C_{60} (**6**) dyads. They found that while the electronic distribution favors through-bond communication in the β-alkynylZnP-C_{60} dyad (**5a**–**c**), the *para*-phenylalkynylZnP-C_{60} (**6**) shows a much slower charge recombination process due, at least in part, to unfavorable orbital interactions between the ZnP and the C_{60} moieties (Fig. 1).

As the β values obtained in TPP-*o*PPV-C_{60} systems (**4**) are still very low (~0.03 Å^{-1}), the objective of this paper is to study eT processes in β-P-*o*PPV-C_{60} triads and to assess the *para* conjugation along the *p*-phenylenevinylene dimer as a π-conjugated system of precise length, and using the free-base and Zn-porphyrins as electron donors. The efficiency in the formation of the radical pairs will determine a further study with other related *p*-conjugated oligomers of different lengths.

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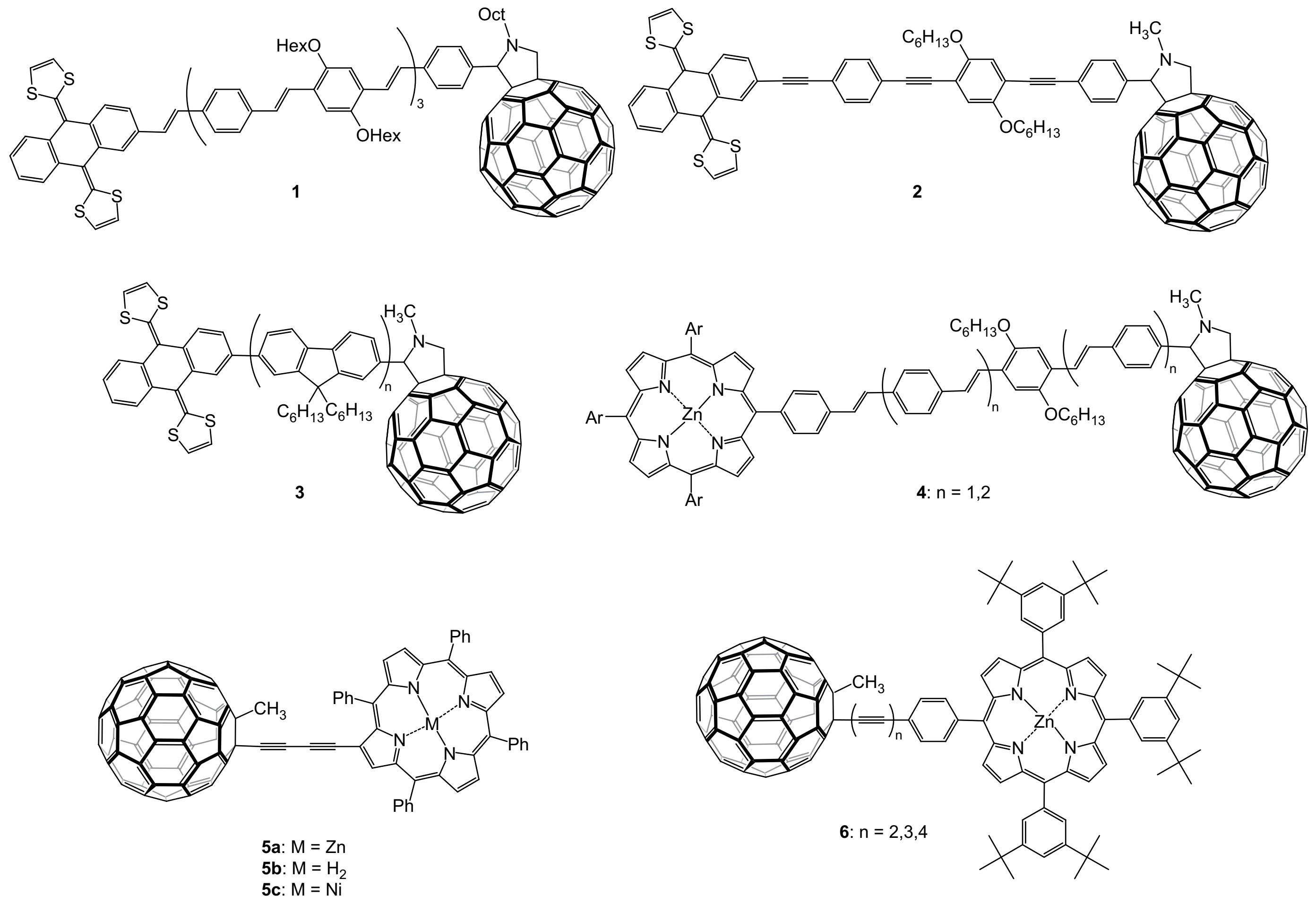


Figure 1. Some fullerene-containing representative DBA examples for the assessment of the molecular wire behavior of the π-conjugated oligomers.

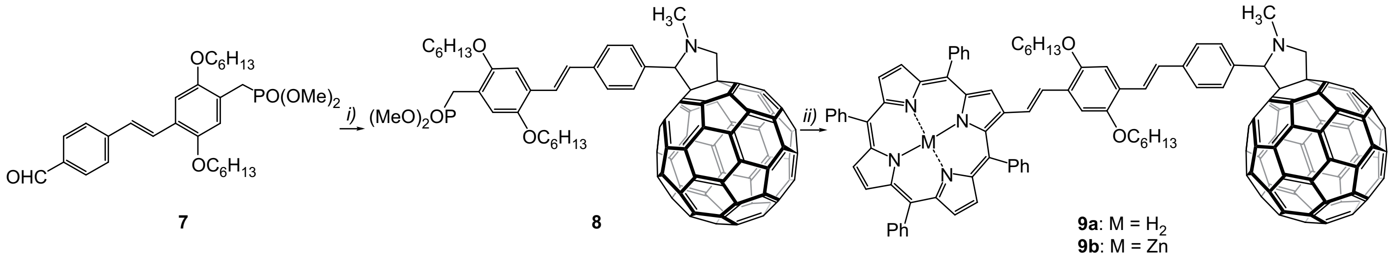
2. Results and discussion

2.1. Synthesis

The synthesis of the new derivatives was carried out as depicted in Scheme 1.

H_2P-*o*PPV-C_{60} (**9a**) and ZnP-*o*PPV-C_{60} (**9b**) triads were synthesized by olefination of porphyrin aldehydes with C_{60}-*o*PPV-phosphonate (**8**). This new *o*PPV-C_{60} phosphonate (**8**) was prepared by 1,3-dipolar cycloaddition of the formyl-*o*PPV-phosphonate (**7**), previously reported in our group,[5b] to C_{60} following Prato's procedure.[10] Phosphonate derivative **8** was thus obtained in 55% yield. By Wadsworth–Emmons olefination reaction of porphyrin aldehydes H_2P-CHO or ZnP-CHO[11] with C_{60}-*o*PPV-phosphonate (**8**), triads H_2P-*o*PPV-C_{60} (**9a**) and ZnP-*o*PPV-C_{60} (**9b**) were synthesized in 18% and 41% yields, respectively. This is, to the best of our knowledge, the first time that the Wadsworth–Emmons reaction has been carried out using a fullerene derivative.

The structures of the new compounds were confirmed by a number of spectroscopic techniques (NMR, FTIR, MS). The ^{1}H NMR spectrum of **8** shows the characteristic signals for the pyrrolidine ring as two doublets at δ ~5.01 and 4.28 with coupling constants of 9.3 Hz, and one singlet at δ ~4.96. The methyl groups of the phosphonate are observed as a doublet at δ ~3.69 with $^3J_{H,P}$ of 10.8 Hz, and the CH_2 in α of the phosphonate unit appears as a doublet at δ ~2.10 with a $^2J_{H,P}$ of 22.1 Hz. For H_2P-*o*PPV-C_{60} (**9a**) and ZnP-*o*PPV-C_{60} (**9b**) triads, the ^{1}H NMR spectra show signals around 9 ppm for the pyrrolic protons of the porphyrin core. A trans



Scheme 1. (i) C_{60}/sarcosine, ClPh/Δ; (ii) H_2P-CHO or ZnP-CHO/^{t}BuOK/THF.

configuration of the vinyl protons of the new formed double bond, with $J \sim 16$ Hz, was observed, as expected from the stereoselectivity of the Wadsworth–Emmons reaction.

The absorption spectra of **9a** and **9b** in CH_2Cl_2 reveal a linear combination of the spectra of H_2P or ZnP and C_{60} components.

Remarkably, compound **8** is an interesting building block, which opens up the possibility of employing the Wadsworth–Emmons reaction in fullerene chemistry.

2.2. Electrochemistry

The electrochemical features of new compounds were studied by cyclic voltammetry at room temperature, in ODCB/CH_3CN 4:1 as the solvent. The obtained redox potentials for **9a** and **9b** are collected in Table 1, together with the phosphonate derivative **8** and tetraphenyl porphyrin as reference compounds.

For compound **8**, three reduction waves corresponding to the first three reductions of the fullerene unit were observed. These waves are shifted to more negative potentials than the parent C_{60}, as a consequence of the saturation of a double bond in the C_{60} cage.[12]

Compounds **9a**,**b** show an amphoteric redox behavior with waves under both oxidation and reduction. Compound **9b** exhibits two oxidation waves at potentials similar to those observed for the reference TPP.[13] In the reduction part, four quasi-reversible waves are observed.[12] The first and second reduction waves correspond to the first two reductions of the C_{60} moiety. The third wave may be assigned to the first reduction of the porphyrin while the fourth should correspond to the third reduction of the fullerene together with the second reduction of the porphyrin subunit, as suggested by the higher intensity of the peak. For compound **9a** the oxidation waves could not be detected owing to their low intensity. On the reduction side, however, five quasi-reversible reduction waves were observed, corresponding to the three reductions of C_{60} and the two reduction peaks of the porphyrin moiety (Fig. 2).

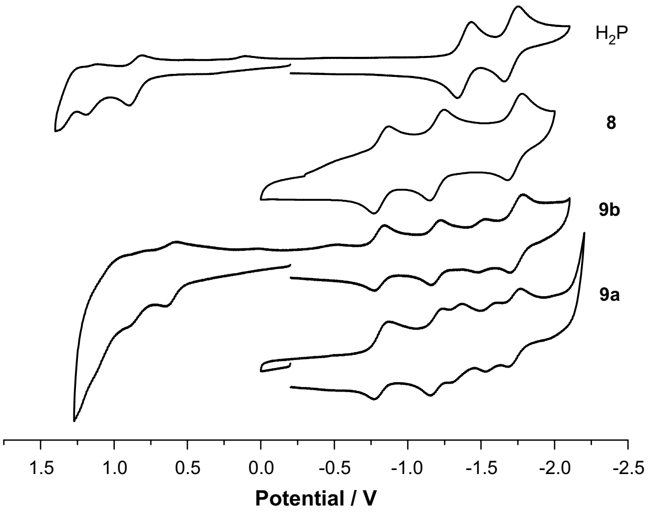


Figure 2. Cyclic voltammograms of H_2P, **8**, and **9a**,**b**.

2.3. Photophysics

2.3.1. Reference compounds

In steady-state experiments, all reference compounds (i.e., C_{60}, oligo-PPV, ZnP/H_2P) emit singlet excited state energy in, however, different spectral regions of the solar spectrum. While the fluorescence of oligo-PPV is typically observed in the 400–500 nm range, ZnP/H_2P emit in the 600–700 nm range, and C_{60} emits with a maximum at 715 nm. The quantum yields vary substantially with values that range between 0.2 and 6×10^{-4} for the H_2P and C_{60} reference, respectively.

Also characteristic features were recorded in our ultrafast and fast transient absorption experiments. We see, for example, singlet excited states that are formed instantaneously: in case of the oligo-PPV singlet-singlet absorptions develop with maxima in the 500–700 nm region (range). Characteristics for ZnP/H_2P are 480 nm. For the C_{60} reference, on the other hand, the maximum is in the red at 880 nm. A fast intersystem crossing process (i.e., in the range of $10^8\ s^{-1}$) governs the fate of the metastable singlet excited states in all references (i.e., C_{60}, oligo-PPV, ZnP/H_2P). The correspondingly formed triplet–triplet absorptions are all located in the range between 500 and 900 nm.

Table 1
Redox potentials at room temperature (in V vs Ag/Ag^+)[a]

Compd	$E^{1,ox}$	$E^{2,ox}$	$E^{1,red}$	$E^{2,red}$	$E^{3,red}$	$E^{4,red}$	$E^{5,red}$
C_{60}			−0.72	−1.12	−1.60		
8	—	—	−0.86	−1.24	−1.78	—	—
H_2P	0.89	1.18	−1.43	−1.75	—	—	—
9a			−0.86	−1.23	−1.36	−1.60	−1.77
9b	0.65	0.88	−0.84	−1.22	−1.52	−1.78	

[a] GCE (glassy carbon) as working electrode, Ag/$AgNO_3$ as reference electrode, Bu_4NClO_4 (0.1 M) as supporting electrolyte, and ODCB/CH_3CN 4:1 (v/v) as solvent. Scan rate 100 mV s^{-1}.

2.3.2. H_2P-oPPV-C_{60}/ZnP-oPPV-C_{60}

In contrast to previously studied C_{60}-oligo-PPE-donor systems,[5] ZnP and H_2P not only absorb notably in the current C_{60}-oligo-PPV-donor systems, but their strong fluorescence dominates large parts of the spectrum (Fig. 3). Interestingly, the ZnP/H_2P centered fluorescence is appreciably quenched in all ZnP-*o*PPV-C_{60} (5.4×10^{-3}–2.6×10^{-3})/H_2P-*o*PPV-C_{60} (0.06–0.03)—regardless of the excitation wavelength (i.e., Soret- or Q-band region)—prompting to the fact that C_{60} must enhance the fluorescence deactivation (vide infra). Interestingly, increasing the solvent polarity intensifies the quenching.

To shed light on the nature of the product, evolving from this intramolecular deactivation, complementary time-resolved transient absorption measurements were necessary. In transient absorption measurements, we focused exclusively on the generation of the singlet excited states of ZnP/H_2P. The overlapping absorptions of all components renders any other analysis ambiguous, though we

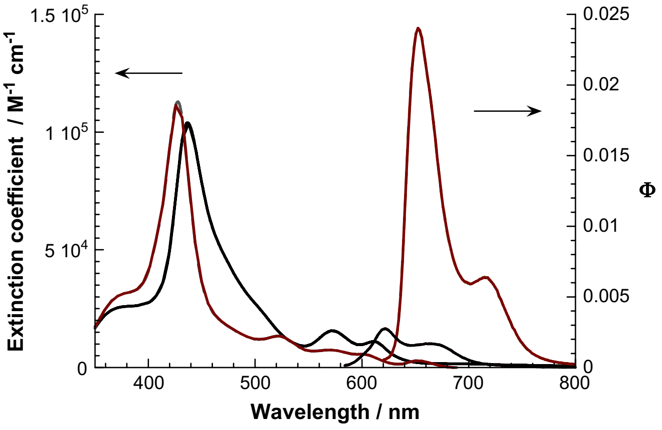


Figure 3. Normalized Absorption and emission spectra of H_2P-*o*PPV-C_{60} (red color) and ZnP-*o*PPV-C_{60} (black color) in benzonitrile at room temperature.

must assume in accordance with previous work that starting with the C_{60} singlet excited state a similar reaction pattern will evolve.[5]

Instead of seeing, however, the slow intersystem crossing dynamics, as the ZnP (i.e., 2.1 ns)/H_2P (i.e., 10.1 ns) references, the singlet–singlet absorption decays in the presence of C_{60} with accelerated dynamics. The singlet excited state lifetimes, as they were determined from an average of first-order fits of the time-absorption profiles at various wavelengths (850–950 nm) are in the range of 0.49 ns (i.e, H_2P-*o*PPV-C_{60}) to 0.19 ns (i.e., ZnP-*o*PPV-C_{60}). Spectroscopically, the transient absorption changes, taken after the completion of the decay, bear no resemblance with any triplet excited state—see Figure 4. Again, varying the solvent polarity from *ortho*-dichlorobenzene to benzonitrile leads to an acceleration of the singlet deactivation: ZnP-*o*PPV-C_{60} (0.09 and 0.07 ns), H_2P-*o*PPV-C_{60} (0.31 and 0.26 ns). This supports our earlier hypothesis that an intramolecular electron transfer, yielding $ZnP^{\bullet+}$-*o*PPV-$C_{60}^{\bullet-}$/$H_2P^{\bullet+}$-*o*PPV-$C_{60}^{\bullet-}$, governs the ZnP/H_2P singlet excited state deactivation.

Spectroscopic evidence for the radical pair formation was provided by the features developing in parallel with the disappearance of the ZnP/H_2P singlet–singlet absorption—see Figure 4. In the visible region, the observed maxima between 500 and 700 nm as well as 480 nm correspond to the one-electron oxidized π-radical cations of ZnP ($ZnP^{\bullet+}$) and H_2P ($H_2P^{\bullet+}$), respectively,[14] while in the near-infrared region, the 1000 nm maximum resembles the signature of the one-electron reduced form of C_{60} ($C_{60}^{\bullet-}$).[15]

3. Conclusions

In summary, we have synthesized two new dyads connected through a *p*-phenylenevinylene dimer as *p*-conjugated system and determined their amphoteric redox character. Photophysical studies reveal that these molecules undergo an efficient electron transfer process upon light irradiation affording the respective charge separated states. These results confirm that β-substitution on a porphyrin moiety results in good electronic coupling and facilitates electronic communication between the donor and acceptor units. Work is currently in progress to prepare related systems with a different length of the *p*-phenylenevinylene oligomer to determine the *β* value for these β-substituted systems.

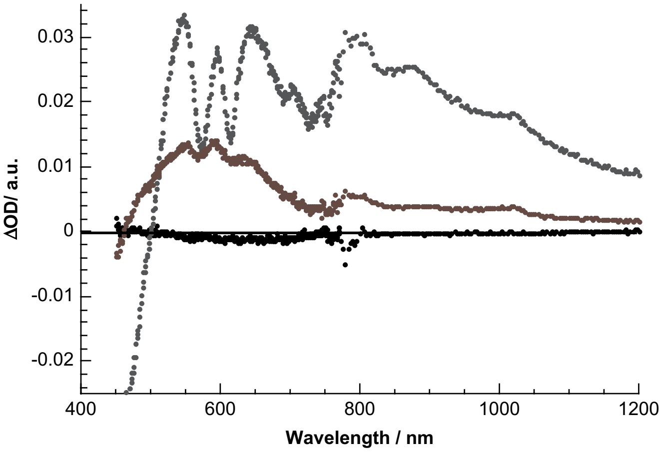


Figure 4. Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (387 nm) of ZnP-*o*PPV-C_{60} in nitrogen saturated benzonitrile with several time delays (i.e., 1 ps, black spectrum; 10 ps, gray spectrum; 300 ps, brown spectrum) at room temperature.

4. Experimental

4.1. Photophysical experiments

UV–vis spectra were recorded on a Varian Cary 50 Scan spectrophotometer in toluene solution. Steady-state fluorescence studies were carried out on a Fluoromax-3 (Horiba) instrument and all spectra were corrected for the instrument response. The femtosecond transient absorption studies were performed with 387 nm laser pulses (1 Khz 150 fs pulse width, 200 mJ) from an amplified Ti:sapphire laser system (Model CPA 2101, Clark-MXR Inc.). Fluorescence quantum yields Φ_F were determined according to the comparative method of Williams et al.[16] We have used the corresponding tetraphenyl porphyrins (free-base and zinc) with their known quantum yields as standard samples. The quantum yields Φ_F have been calculated according to

$$\Phi_F = \Phi_{FR}\frac{I}{I_R}\frac{OD_R}{OD}\frac{n^2}{n_R^2}$$

where Φ_F is the quantum yield, *I* is the integrated intensity, *n* is the refractive index, and OD is the optical density. The subscript R refers to the tetraphenyl porphyrin reference fluorophore of known quantum yield.

4.1.1. *Synthesis of compound **8***

A solution of C_{60} (348 mg, 0.483 mmol), {4-[2-(4-diethoxymethylphenyl)vinyl]-2,5-bishexyloxybenzyl} dimethyl phosphonate **7** (64 mg, 0.12 mmol), and sarcosine (53 mg, 0.60 mmol) was refluxed in chlorobenzene (100 mL) for 5 h. The solvent was removed under reduced pressure and the crude material was carefully chromatographed over silica using carbon disulfide, toluene, and toluene/acetonitrile 19:1 as eluents. Further purification was accomplished by repetitive precipitation and centrifugation by using cyclohexane as solvent (85 mg, 55%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.79 (br s, 2H), 7.59 (d, *J*=7.9 Hz, 2H), 7.47 (d, *J*=16.4 Hz, 1H), 7.09 (d, *J*=16.4 Hz, 1H), 7.06 (s, 1H), 6.91 (d, *J*=2.5 Hz, 1H), 5.01 (d, *J*=9.3 Hz, 1H), 4.96 (s, 1H), 4.28 (d, *J*=9.3 Hz, 1H), 3.98 (t, *J*=6.4 Hz, 4H), 3.69 (d, *J*=10.8 Hz, 6H), 2.10 (d, *J*=22.1 Hz, 2H), 2.84 (s, 3H), 1.85–1.79 (m, 4H), 1.51–1.48 (m, 4H), 1.36–1.34 (m, 8H), 0.92–0.90 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ=156.68, 154.47, 153.88, 153.80, 151.24, 151.14, 151.00, 150.95, 147.71, 147.19, 146.89, 146.72, 146.63, 146.55, 146.51, 146.34, 146.18, 145.95, 145.88, 145.72, 145.66, 145.56, 145.11, 145.01, 144.80, 143.55, 143.39, 143.09, 142.98, 142.68, 142.66, 142.54, 142.47, 142.44, 142.41, 142.34, 142.26, 142.09, 141.94, 140.58, 140.55, 140.29, 139.98, 138.45, 137.22, 136.94, 136.49, 136.25, 136.15, 130.02, 128.63, 127.14, 126.32, 126.26, 124.37, 120.82, 120.69, 116.29, 116.22, 110.10, 83.86, 70.46, 69.83, 69.49, 53.20, 53.11, 40.47, 32.03, 32.00, 29.85, 29.76, 26.29, 26.20, 23.05, 14.48, 14.45. HR-MALDI-TOF: calcd for $C_{92}H_{49}NO_5P$: 1278.3343, found: 1278.3331. FTIR (KBr) ν (cm^{-1}) 3452, 2924, 2853, 2779, 1628, 1498, 1463, 1420, 1209, 1057, 1033, 868, 527. UV–vis ($CHCl_3$) λ_{max} (nm) 430, 373, 307, 255, 231.

4.1.2. *Synthesis of compound **9a***

To a stirred solution of **8** (50 mg, 0.039 mmol) and H_2P-CHO (25 mg, 0.039 mmol) in anhydrous THF (20 mL), potassium *tert*-butoxide (6.5 mg, 0.058 mmol) was added under argon atmosphere. The resulting solution was refluxed overnight. Methanol (5 mL) and water (25 mL) were added. The mixture was extracted with chloroform and the organic layer dried over sodium sulfate. The solvent was removed under reduced pressure and the resulting residue was chromatographed on a silica gel column, using carbon disulfide/dichloromethane 4:1 as eluent. Compound **9a** (12.7 mg, 18%) was thus obtained as a black solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ=9.05 (s, 1H), 8.85–8.80 (m, 4H), 8.76 (d, *J*=4.8 Hz, 1H), 8.66 (d,

J=4.8 Hz, 1H), 8.27–8.20 (m, 8H), 7.85–7.76 (m, 14H), 7.65 (d, J=7.8 Hz, 2H), 7.45 (d, J=16.4 Hz, 1H), 7.16 (d, J=16.4 Hz, 1H), 7.11 (s, 1H), 6.91 (d, J=16.2 Hz, 1H), 6.68 (s, 1H), 4.89 (d, J=9.3 Hz, 1H), 4.84 (s, 1H), 4.15 (d, J=9.3 Hz, 1H), 4.11 (t, J=6.5 Hz, 2H), 4.04 (t, J=6.5 Hz, 2H), 2.81 (s, 3H), 2.05–2.00 (m, 2H), 1.90–1.85 (m, 2H), 1.74–1.70 (m, 2H), 1.41–1.39 (m, 8H), 1.02–0.96 (m, 6H), −2.56 (br s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ=156.53, 154.27, 153.73, 153.68, 151.59, 151.39, 147.48, 147.08, 146.68, 146.51, 146.42, 146.16, 146.01, 145.77, 145.68, 145.56, 145.37, 144.90, 144.62, 143.37, 143.21, 143.04, 142.93, 142.80, 142.73, 142.48, 142.37, 142.25, 142.15, 141.85, 140.40, 140.20, 139.91, 139.35, 139.19, 138.62, 137.16, 136.81, 136.52, 136.12, 135.99, 135.05, 135.02, 134.94, 134.88, 134.54, 130.49, 130.27, 130.12, 129.04, 128.70, 128.52, 128.11, 127.91, 127.33, 127.21, 127.10, 127.01, 126.83, 125.32, 124.87, 124.46, 123.97, 120.91, 120.34, 120.25, 120.13, 111.05, 110.53, 109.92, 83.86, 70.45, 70.24, 69.96, 69.38, 40.46, 32.32, 32.08, 30.23, 29.89, 26.69, 26.33, 23.32, 23.19, 14.68, 14.65. HR-MALDI-TOF: calcd for $C_{135}H_{72}N_5O_2$: 1794.5681, found 1794.5653. FTIR (KBr) ν (cm^{-1}) 3443, 2923, 2852, 1599, 1463, 798, 527. UV–vis ($CHCl_3$) λ_{max} (nm) 655, 602, 570, 519, 422, 327, 255.

4.1.3. *Synthesis of compound* ***9b***

To a stirred solution of **8** (45 mg, 0.035 mmol) and ZnP-CHO (25 mg, 0.035 mmol) in anhydrous THF (20 mL), potassium *tert*-butoxide (5 mg, 0.043 mmol) was added under argon. After refluxing overnight, methanol (5 mL) and water (25 mL) were added. The mixture was extracted with chloroform and the organic layer dried over sodium sulfate. The solvent was removed under reduced pressure and the resulting residue was chromatographed on a silica gel column, using carbon disulfide/dichloromethane 4:1 as eluent. Compound **9b** (27.1 mg, 41%) was thus obtained as a black solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ=9.13 (s, 1H), 8.96–8.91 (m, 4H), 8.88 (d, J=4.6 Hz, 1H), 4.77 (d, J=4.6 Hz, 1H), 8.27–8.26 (m, 2H), 8.23–8.20 (m, 6H), 7.80–7.72 (m, 14H), 7.61 (d, J=7.3 Hz, 2H), 7.51 (d, J=16.4 Hz, 1H), 7.13 (d, J=16.4 Hz, 1H), 7.07 (s, 1H), 6.92 (d, J=16.1 Hz, 1H), 6.66 (s, 1H), 4.98 (d, J=9.3 Hz, 1H), 4.93 (s, 1H), 4.25 (d, J=9.3 Hz, 1H), 4.10 (t, J=6.5 Hz, 2H), 4.04 (t, J=6.5 Hz, 2H), 2.87 (s, 3H), 2.05–2.01 (m, 2H), 1.90–1.87 (m, 2H), 1.75–1.72 (m, 4H), 1.45–1.42 (m, 8H), 1.02–0.96 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ=151.56, 151.45, 151.32, 151.02, 150.85, 150.80, 150.69, 150.46, 149.46, 147.57, 147.41, 147.12, 146.73, 146.62, 146.50, 146.44, 146.22, 146.07, 145.80, 145.72, 145.61, 144.97, 144.68, 143.73, 143.41, 143.26, 143.18, 142.98, 142.86, 142.51, 142.42, 142.35, 142.29, 141.90, 140.49, 139.98, 134.93, 134.83, 134.71, 132.72, 132.66, 132.56, 132.37, 131.98, 130.69, 130.03, 128.76, 128.47, 128.34, 128.22, 127.93, 127.20, 127.04, 127.02, 126.95, 124.94, 124.68, 124.54, 122.02, 121.47, 121.36, 120.95, 110.99, 110.00, 83.89, 70.47, 70.25, 69.94, 69.39, 40.48, 32.36, 32.15, 30.29, 29.95, 26.75, 26.37, 23.39, 23.32, 14.69. HR-MALDI-TOF: calcd for $C_{135}H_{69}N_5O_2Zn$: 1855.4737, found 1855.4758. FTIR (KBr) ν (cm^{-1}) 3452, 2922, 2851, 1636, 1464, 1003, 795, 700, 526. UV–vis ($CHCl_3$) λ_{max} (nm) 599, 558, 425, 328, 255.

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