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Rational synthetic design of well-defined Pt(bisethynyl)/Zn(porphyrin) oligomers for potential applications in photonics[†]‡

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Well-defined oligomers of 1, 2, 3 and 4 units built upon the very soluble bis-1,15-(1.4-ethynylbenzene)-3,7,13,17-tetramethyl-2,8,12,18-tetrakis(n-hexyl) zinc(II) porphyrin ligand and the *trans*-bis(tri-n-butylphosphine)platinum(Π) linker, with acetylene or trimethylsilane as end groups, has been prepared in the presence of a dichloromethane/diethylamine mixture (1:1 v/v)and CuX (X = Cl, I) at room temperature, analogue to a Sonogashira coupling. The new monodisperse organometallic oligomers were characterized by ¹H, ³¹P NMR, UV-visible spectroscopies and MALDI-TOF mass spectrometry. The methyl groups placed at the 3,7,13,17-positions induces the locking of the C_6H_4 fragment in a perpendicular conformation with respect to the zinc(II) porphyrin chromophore, hence removing conjugation as corroborated by the almost total absence of spectral shift of the Soret and Q-bands upon increasing the number of units. Despite this feature, exciton coupling in the Soret band is noted at both room temperature and 77 K. The photophysical parameters, fluorescence lifetimes and quantum yields are practically constant going from the monomer, dimer and tetramer, and as a function of the monitored fluorescence wavelength, all indicating that the excitonic behavior (excitation energy delocalization) is minimal, which is consistent with the weak exciton coupling constants and the lack of conjugation of the π -system. The synthetic methodology can provide longer well-defined oligomers as the presented products were still very soluble even when the number of unit was 4.

Introduction

The conjugated polyporphyrin assemblies covalently held by ethynyl bridges for photonic applications have gained an important place in the design of light harvesting devices and long-distance electron transports.^{1–3} The investigations of the corresponding analogous organometallic version of such assemblies, notably using platinum bisethynyl linkers, *trans*- $C \equiv C-PtL_2-C \equiv C$ (L = PEt₃, PBu₃), are just in its infancy based on a recent review.⁴ The mononuclear *trans*- $ArC \equiv C-PtL_2-C \equiv CAr$ (Ar = aromatic) species are wellknown for non-linear⁵ and two-photon absorption properties,⁶ electronic communication across the backbone,⁷ luminescence (notably phosphorescence)⁸ with occasional excimer formations.⁹ All these properties can also be found in the oligomers (mono- and polydispersed),^{10,11} and applications of sensorisation of transition metals,¹² charge separation,¹³ light emitting diodes^{14,15} and photocells were reported as well.¹⁶⁻¹⁹

Indeed, the earlier syntheses of species, monomers and oligomers of Pt(bisethynyl)/Zn(porphyrin) systems, were reported by Russo and collaborators in 2003 and 2004 (Chart 1),^{20–22} latter by Chen and collaborators (2006),²³ and more recently by us over the past two years (Chart 1),^{24–26} including systems where the metal-metal-bonded Pt₂(dppm)₂ bridge is used.²⁷ Solubility is a major challenge in these cases, and so the growth of longer chain appears challenging at first glance. On the photophysical point of view, evidence for electronic communications across the oligomers such as conjugation, singlet and triplet energy transfer and long-distance heavy atom effect is provided.

One common point is that in attempts to prepare long polymer chains from the conventional ligand substitution

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[‡] Electronic supplementary information (ESI) available: MALDI/ TOF mass spectrum of the reaction mixture during the one-pot reaction of **1b** with PtCl₂(PBu₃)₂ (Fig. S1), ¹H and ³¹P NMR spectra of the different oligomers and precursors (Fig. S2–13), MALDI/TOF MS spectra of the different oligomers and precursors (Fig. S14–31) and IR spectra (KBr) of the different oligomers (Fig. S32–S38). See DOI: 10.1039/c0nj00819b

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strategy "Pt–Cl" + H–C \equiv CR (with a small amount of CuI) leads only to short and polydispersed oligomers (PD are in the order of 1.5 to 2.0 based on GPC analysis). The downfall is that when comes the photophysical characterization of such 1D-oligomeric species, one cannot be certain what is the main contributor to the photophysical parameters such as emission lifetimes and quantum yields. The need to find an easy strategy to prepare any oligomers of a well-defined length is crucial in the structure-properties relationship.

We now wish to report the syntheses of easily accessible and well-defined oligomers (monomers, dimers, trimer and tetramer; Chart 2 and 3) of Pt(bisethynyl)/Zn(porphyrin) systems, where



the incorporation of soluble groups such as hexyls at the β -position and the control of the stoichiometry of the reactants are made. The photophysical properties of representative examples are investigated and the data are in the same range of previously reported other polydispersed oligomers of the similar type.^{25,26} A weak excitonic coupling is noticed in the Soret bands and a suspected very small increase in internal conversion rate constant in the S₁ state appears responsible to the very small decrease in fluorescence lifetimes as the oligomer length increases.

Experimental section

Materials

The porphyrin precursors, **1a** and **1b**, were synthesized as previously reported.^{28,29} The following materials were purchased from commercial suppliers: DDQ (dichlorodicyanoquinone; Aldrich), triethylphosphine (Aldrich), diisopropylamine (Aldrich), phenylacetylene (Aldrich), copper(1) iodide (Aldrich), [(trimethylsilyl)ethynyl]benzaldehyde (Aldrich), dichloromethane (EMD), platinum(II) chloride (Strem), potassium carbonate (Fisher), ether (ACP), hexane (ACP), ethanol (Commercial Alcohols inc.). All the solvents were purified according to literature procedures. The coupling reactions were performed under nitrogen using Schlenk techniques, with flame dried reaction vessels before use. Silica gel (Merck; 70–120 μ m) was used for column chromatography. Analytical thin layer chromatography was performed using Merck 60 F₂₅₄ silica





gel (precoated sheets, 0.2 mm thick). All the reactions were monitored by thin-layer chromatography and UV-visible spectroscopy.

5,15-Bis(trans-bis(1,4-ethynylbenzene)bis(tri-n-butylphosphine)platinum(II))-3,7,13,17-tetramethyl-2,8,12,18-tetrakis(n-hexyl)-Zinc(II)porphyrin (4). A mixture of the porphyrin 1b (15.0 mg, 15.5 µmol), trans-phenylethynyl-chlorobis(tri-n-butylphosphine)platinum(II) (24.0 mg, 32.6 µmol), and CuI (1.0 mg, 5.3 µmol) was dissolved in CH_2Cl_2/Et_2NH (4 mL, 1:1 v/v). The mixture was stirred at room temperature for 15 min. After removal of the solvent in vacuo, the resulting mixture was recrystallized (CH₂Cl₂-CH₃OH). The red solid was washed with CH₃OH and collected with CH₂Cl₂. The solvent was evaporated in vacuo and the red solid was recrystallized a second time (CH₂Cl₂-CH₃OH) to afford **4** as a red solid in 87% yield (31.8 mg, 13.4 μ mol). HR-MS (MALDI-TOF): m/z =2363.3119 $[M]^{+\bullet}$ 2363.2684 calcd for $C_{128}H_{192}N_4P_4Pt_2Zn$. ^{31}P NMR (161.92 MHz, CHCl₃) δ (ppm): 3.20. ^{1}H NMR (300 MHz, CDCl₃) δ (ppm): 10.17 (s, 2H, H-meso), 7.88 (d, 4H, ${}^{3}J_{H-H} = 8.0$ Hz, Ph), 7.64 (d, 4H, ${}^{3}J_{H-H} = 8.0$ Hz, Ph), 7.32 (d, 6H, ${}^{3}J_{H-H} = 8.0$ Hz, Ph), 7.23 (d, 4H, ${}^{3}J_{H-H} = 8.0$ Hz, Ph), 3.97 (t, 8H, ${}^{3}J_{H-H} = 7.2$ Hz, CH₂), 2.54 (s, 12H, CH₃), 2.30–2.08 (m, 32H, CH₂), 1.81–1.68 (m, 32H, CH₂), 1.62–1.32 (m, 40H, CH₂), 1.02 (t, 36H ${}^{3}J_{H-H} = 7.2$ Hz, CH₃), 0.91 (t, 12H, ${}^{3}J_{H-H} = 7.2$ Hz, CH₃).

Trans-chloro-[5-(4-ethynylphenyl)-15-[4-(trimethylsilyl)ethynylphenyl]-3,7,13,17-tetramethyl-2,8,12,18-tetrakis-(n-hexyl)-zinc(II)porphyrin|bis(tri-n-butyl-phosphine)-platinum(II) (3a). A mixture of trans-bis(tri-n-butylphosphine)-dichloro-platinum(II) (152.4 mg, 227.3 µmol) and CuI (5.1 mg, 27 µmol) was solubilized in a mixture of CH_2Cl_2/Et_2NH (15 mL, 1:1 v/v). The porphyrin 1c (117.2 mg, 56.4 µmol) was solubilized in CH₂Cl₂ (15 mL) and added dropwise over 1 h at room temperature. After 30 min of additional stirring, the solvents were removed in vacuo to afford a red solid. The porphyrin 1c and *trans*-bis(tri-n-butylphosphine)dichloro-platinum(II) were partially removed by fractional crystallization (CH₂Cl₂-CH₃OH). The solvents of the fraction containing the title compound 3a were removed in vacuo. The resulting red solid was purified using a solution of CH₂Cl₂pentane (20:80-30:70 v/v) containing 0.5% of Et₃N to afford the title compound 3a as a red solid in 49% yield (45.8 mg, 27.4 μ mol). HR-MS (MALDI-TOF): $m/z = 1669.8837 \text{ [M]}^{+\bullet}$ 1669.8715 calcd for $C_{91}H_{137}ClN_4P_2PtSiZn$. ³¹P NMR (161.92 MHz, CHCl₃) δ (ppm): 8.15. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 10.17 (s, 2H, H-meso), 8.04 (d, 2H, ${}^{3}J_{H-H} = 8.0$ Hz, Ph), 7.89 (d, 2H, ${}^{3}J_{H-H} = 8.0$ Hz, Ph), 7.86 (d, 2H, ${}^{3}J_{H-H} = 8.0$ Hz, Ph), 7.61 (d, 2H, ${}^{3}J_{H-H} = 8.0$ Hz, Ph), 4.00–4.93 (br, 12H, CH₂), 2.53 (s, 6H, CH₃), 2.47 (s, 6H, CH₃), 2.22-2.11 (br, 16H, CH₂), 1.77–1.66 (br, 16H, CH₂), 1.56 (sextet, 16H, ${}^{3}J_{H-H}$ = 7.3 Hz, CH₂), 1.49 (quintet, 8H, ${}^{3}J_{H-H} = 7.3$ Hz, CH₂), 1.38

(quintet, 8H, ${}^{3}J_{H-H} = 7.3$ Hz, CH₂), 1.02 (t, 18H, ${}^{3}J_{H-H} = 7.3$ Hz, CH₂), 0.91 (t, 12H, ${}^{3}J_{H-H} = 7.3$ Hz, CH₂), 0.40 (s, 9H, Si(CH₃)₃).

Trans-(4-Ethynylphenyl)-[5-(4-ethynylphenyl)-15-[4-(trimethylsilyl)-ethynyl-phenyl]-3,7,13,17-tetramethyl-2,8,12,18-tetrakis-(n-hexyl)-zinc(II)-porphyrin]-bis(tri-n-butylphosphine)-platinum(II) (2a). The porphyrin 1c (91.2 mg, 43.9 µmol), trans-phenylethynyl-chlorobis(tri-n-butylphosphine)platinum(II) (38.5 mg, 52.3 µmol) and CuI (8.0 mg, 42.0 µmol) were dissolved in CH_2Cl_2/Et_2NH (12 mL,1:1 v/v). The reaction mixture was stirred at room temperature for 10 min and was monitored by TLC. The solvent was removed in vacuo and the residue was purified by silica gel chromatography (30:60 CH₂Cl₂/ heptane). The resulting red solid was recrystallized (CH₂Cl₂-CH₃OH) to afford the title compound 2a as a red solid in 66% yield (50.0 mg, 28.8 µmol). HR-MS (MALDI-TOF): $m/z = 1735.9453 \text{ [M]}^{+\bullet} 1735.9418 \text{ calcd for } C_{99}H_{142}N_4P_2$ PtSiZn. This intermediate was not further characterized and was used directly in the following deprotection step.

Trans-(4-Ethynylphenyl)-[5,15-bis(4-ethynylphenyl)-3,7,13,17tetramethyl-2,8,12,18-tetrakis(n-hexyl)zinc(II)porphyrinlbis(tri-nbutylphosphine)platinum(II) (2b). The porphyrin 2a (49.8 mg, 28.6 µmol) was dissolved in tetrahydrofuran (20 mL). NBu₄F (200 µL, 1.0 M in THF) was added and the mixture was stirred at room temperature for 1 h. The solvent was removed in vacuo. The resulting red solid was recrystallized (CH₂Cl₂-CH₃OH). The red solid was washed with CH₃OH and collected with CH₂Cl₂. The solvent was evaporated in vacuo and the red solid was recrystallized a second time to afford the title compound 2b as a red cotton-like microcrystalline solid in 77% yield (36.8 mg, 22.1 μ mol). HR-MS (MALDI-TOF): $m/z = 1663.9088 \, [M]^{+}$ 1663.9023 calcd for C₉₆H₁₃₄N₄P₂PtZn. ³¹P NMR (161.92 MHz, CHCl₃) δ (ppm): 4.27. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 10.17 (s, 2H, H-meso), 8.06 (d, 2H, ${}^{3}J_{H-H} = 8.0$ Hz, Ph), 7.89 (d, 2H, ${}^{3}J_{H-H} = 8.0$ Hz, Ph), 7.87 (d, 2H, ${}^{3}J_{H-H} = 8.0$ Hz, Ph), 7.65 (d, 2H, ${}^{3}J_{H-H} = 8.0$ Hz, Ph), 7.32 (d, 2H, ${}^{3}J_{H-H} = 7.3$ Hz, Ph), 7.23 (d, 2H, ${}^{3}J_{H-H} = 7.3$ Hz, Ph), 7.15 (d, 1H, ${}^{3}J_{H-H} = 7.3$ Hz, Ph), 4.00-3.91 (br, 12H, CH₂), 3.33 (s, 1H, CH), 2.54 (s, 6H, CH₃), 2.47 (s, 6H, CH₃), 2.25–2.33 (br, 8H, CH₂), 2.17 (sextet, 8H, ${}^{3}J_{H-H} =$ 7.3 Hz, CH₂), 1.80–1.69 (br, 16H, CH₂), 1.56 (sextet, 16H, ${}^{3}J_{H-H} =$ 7.3 Hz, CH₂), 1.49 (quintet, 8H, ${}^{3}J_{H-H} = 7.3$ Hz, CH₂), 1.39 (quintet, 8H, ${}^{3}J_{H-H} = 7.3$ Hz, CH₂), 1.01 (t, 18H, ${}^{3}J_{H-H} = 7.3$ Hz, CH₃), 0.91 (t, 12H, ${}^{3}J_{H-H} = 7.3$ Hz, CH₃).

Trans-bis-[5-(4-ethynylphenyl)-15-[4-(trimethylsilyl)ethynylphenyl]-3,7,13,17-tetramethyl-2,8,12,18-tetrakis(n-hexyl)zinc(II)porphyrin]bis(tri-n-butylphosphine)-platinum(II) (5a). The porphyrin 1c (70.6 mg, 34.0 µmol), *trans*-dichloro-bis(tri-n-butylphosphine)platinum(II) (10.3 mg, 15.4 µmol) and CuCl (1.0 mg, 10 µmol) were dissolved in CH₂Cl₂/Et₂NH (4.0 mL, 1:1 v/v). The reaction was stirred at room temperature for 20 min and was monitored by TLC. The solvent was removed *in vacuo* and the resulting red solid was recrystallized (CH₂Cl₂-CH₃OH). The red solid was washed with CH₃OH and collected with CH₂Cl₂. The solvent was evaporated *in vacuo* and the red solid was recrystallized a second time to afford the title compound **5a** as a red solid in 73% yield (30.0 mg, 11.2 µmol). HR-MS (MALDI-TOF): m/z = 2670.4435[M]^{+•} 2670.4705 calcd for C₁₅₈H₂₂₀N₈P₂PtSi₂Zn₂. ³¹P NMR (161.92 MHz, CHCl₃) δ (ppm): 3.34. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 10.19 (s, 4H, H-*meso*), 8.05 (d, 4H, ${}^{3}J_{H-H} = 8.0$ Hz, Ph), 7.92 (d, 4H, ${}^{3}J_{H-H} = 8.0$ Hz, Ph), 7.88 (d, 4H, ${}^{3}J_{H-H} = 8.0$ Hz, Ph), 7.11 (d, 4H, ${}^{3}J_{H-H} = 8.0$ Hz, Ph), 3.04–3.90 (br, 16H, CH₂), 2.58 (s, 12H, CH₃), 2.49 (s, 12H, CH₃), 2.47–2.49 (br, 12H, CH₂), 2.25–2.12 (br, 16H, CH₂), 1.95–1.83 (br, 12H, CH₂), 1.82–1.70 (br, 16H, CH₂), 1.69 (sextet, 12H, ${}^{3}J_{H-H} = 7.3$ Hz, CH₂), 1.52-1.45 (br, 16H, CH₂), 1.44–1.34 (br, 16H, CH₂), 1.12 (t, 18H, ${}^{3}J_{H-H} = 7.3$ Hz, CH₃), 0.93 (t, 12H, ${}^{3}J_{H-H} = 7.3$ Hz, CH₃), 0.92 (t, 12H, ${}^{3}J_{H-H} = 7.3$ Hz, CH₃), 0.91 (s, 18H, Si(CH₃)₃).

Trans-bis[5,15-bis(4-ethynylphenyl)-3,7,13,17-tetramethyl-2, 8,12,18-tetrakis(n-hexyl)zinc(II)porphyrin|bis(tri-n-butylphosphine)platinum(II) (5b). The porphyrin 5a (30 mg, 11.2 µmol) was dissolved in tetrahydrofuran (8.0 mL). NBu₄F (70 µL, 1.0 M in THF) was added and the mixture was stirred at room temperature for 20 min. The solvent was removed in vacuo. The resulting red solid was recrystallized (CH₂Cl₂-CH₃OH). The red solid was washed with CH₃OH and collected with CH₂Cl₂. The solvent was evaporated in vacuo and the red solid was recrystallized a second time to afford the title compound 5b as a red solid in quantitative yield (28.4 mg, 11.2 µmol). HR-MS (MALDI-TOF): $m/z = 2526.4127 \text{ [M]}^{+\circ} 2526.3915$ calcd for C₁₅₂H₂₀₄N₈P₂PtZn₂. ³¹P NMR (161.92 MHz, CHCl₃) δ (ppm): 4.39. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 10.20 (s, 4H, H-meso), 8.07 (d, 4H, ${}^{3}J_{H-H} = 8.0$ Hz, Ph), 7.92 (d, 4H, ${}^{3}J_{H-H} = 8.0$ Hz, Ph), 7.90 (d, 4H, ${}^{3}J_{H-H} =$ 8.0 Hz, Ph), 7.70 (d, 4H, ${}^{3}J_{H-H} = 8.0$ Hz, Ph), 4.04–3.92 (br, 16H, CH₂), 3.34 (s, 2H, CH), 2.58 (s, 12H, CH₃), 2.48 (s, 12H, CH₃), 2.47-2.42 (br, 12H, CH₂), 2.21-2.13 (br, 16H, CH₂), 1.94–1.84 (br, 12H, CH₂), 1.80–1.70 (br, 16H, CH₂), 1.67 (sextet, 12H, ${}^{3}J_{H-H} = 7.3$ Hz, CH₂), 1.52–1.45 (br, 16H, CH2),1.44–1.35 (br, 16H, CH₂), 1.11 (t, 18H, ${}^{3}J_{H-H} = 7.3$ Hz, CH₃), 0.93 (t, 12H, ${}^{3}J_{H-H} = 7.3$ Hz, CH₃), 0.92 (t, 12H, ${}^{3}J_{H-H} =$ 7.3 Hz, CH₃).

Trans-bis[5-(4-ethynylphenyl)-15-[trans-bis(1,4-ethynylphenyl)bis(tri-n-butyl-phosphine)-platinum(II)]-3,7,13,17-tetramethyl-2,8, 12,18-tetrakis(n-hexyl)-zinc(II)-por-phyrin|bis(tri-n-butylphosphine)platinum(II) (6). A mixture of the porphyrin 2b (8.8 mg, 3.5 µmol), trans-phenylethynyl-chlorobis(tri-n-butylphosphine)platinum(II) (8.0 mg, 10.9 µmol) and CuI (1.0 mg, 5.3 µmol) was dissolved in CH₂Cl₂/Et₂NH (4 mL,1:1 v/v). The mixture was stirred at room temperature for 15 min. After removal of the solvent in vacuo, the resulting mixture was recrystallized (CH₂Cl₂-CH₃OH). The red solid was washed with CH₃OH and collected with CH₂Cl₂. The solvent was evaporated in vacuo and the red solid was recrystallized a second time to afford 6 as a red solid in 84% yield (11.5 mg, 2.92 µmol). HR-MS (MALDI-TOF): $m/z = 3925.1390 \text{ [M]}^{+\bullet} 3925.1238$ calcd for C₂₁₆H₃₂₀N₈P₆Pt₃Zn₂. ³¹P NMR (161.92 MHz, CHCl₃) δ (ppm): 3.34, 3.21. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 10.19 (s, 4H, H-meso), 7.93 (d, 4H, ${}^{3}J_{H-H} = 8.0$ Hz, Ph), 7.90 (d, $4H^{3}_{,3}J_{H-H} = 8.0$ Hz, Ph), 7.69 (d, $4H^{3}_{,3}J_{H-H} = 8.0$ Hz, Ph), 7.65 (d, 4H, ${}^{3}J_{H-H} = 8.0$ Hz, Ph), 7.31 (d, 4H, ${}^{3}J_{H-H} = 8.0$ Hz, Ph), 7.22 (br, 6H, Ph), 4.05-3.92 (br, 16H, CH₂), 2.58 (s, 12H, CH₃), 2.55 (s, 12H, CH₃), 2.50–2.40 (br, 12H, CH₂), 2.35–2.12 (br, 40H, CH₂), 1.95-1.83 (br, 12H, CH₂), 1.82-1.60 (br, 52H, CH₂), 1.60–1.46 (br, 40H, CH2),1.45–1.35 (br, 16H, CH₂), 1.11 (t, 18H, ${}^{3}J_{H-H} = 7.3$ Hz, CH₃), 1.02 (t, 36H, ${}^{3}J_{H-H} = 7.3$ Hz, CH₃),0.93 (t, 12H, ${}^{3}J_{H-H} = 7.3$ Hz, CH₃), 0.92 (t, 12H, ${}^{3}J_{H-H} = 7.3$ Hz, CH₃).

Trans-[5-(4-ethynylphenyl)-15-[trans-bis(1,4-ethynylphenyl)bis(tri-n-butyl-phosphine)-platinum(II)]-3,7,13,17-tetramethyl-2,8,12,18-tetrakis-(n-hexyl)-zinc(II)-porphyrin]-[5-(4-ethynylphenvl)-15-[4-(trimethylsilyl)ethynylphenvl]-3,7,13,17-tetraethyl-2,8,12,18-tetrakis-(n-hexyl)-zinc(II)-porphyrin]-bis(trin-butylphosphine)-platinum(II) (8a). A mixture of porphyrin 3a (35.0 mg, 20.9 µmol), porphyrin 2b (31.5 mg, 18.9 µmol) and CuI (2.0 mg, 10.5 µmol) was dissolved in CH₂Cl₂/Et₂NH (10 mL, 1: 1 v/v). The mixture was stirred at room temperature for 10 min. After removal of the solvent in vacuo, the resulting mixture was recrystallized (CH2Cl2-CH3OH). The red solid was washed with CH₃OH and collected with CH₂Cl₂. The solvent was evaporated in vacuo and the red solid was recrystallized a second time to afford 10 as a red solid in 70% yield (43.5 mg, 13.1 µmol). HR-MS (MALDI-TOF): m/z = 3297.6804 $\label{eq:main_state} [M]^{+\bullet} \ 3297.7972 \ calcd \ for \ C_{187} H_{270} N_8 P_4 P t_2 Si Zn_2. \ ^{31} P \ NMR$ (161.92 MHz, CHCl₃) δ (ppm): 4.39, 4.26. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 10.19 (s, 4H, H-meso), 7.92 (d, 4H, ${}^{3}J_{H-H} =$ 8.0 Hz, Ph), 7.87 (d, 4H, ${}^{3}J_{H-H} = 8.0$ Hz, Ph), 7.70 (d, 4H, ${}^{3}J_{H-H} = 8.0$ Hz, Ph), 7.65 (d, 4H, ${}^{3}J_{H-H} = 8.0$ Hz, Ph), 7.33 (m, 2H, ${}^{3}J_{H-H} = 8.0$ Hz, Ph), 7.23 (m, 3H, ${}^{3}J_{H-H} = 8.0$ Hz, Ph), 3.98 (m, 16H, CH₂), 2.57 (s, 6H, CH₃), 2.55 (s, 6H, CH₃), 2.49 (s, 6H, CH₃), 2.47 (s, 6H, CH₃), 2.46–2.42 (br, 12H, CH₂), 2.33-2.25 (br, 24H, CH₂), 2.23-2.13 (br, 16H, CH₂), 1.94-1.84 (br, 12H, CH₂), 1.80-1.71 (br, 28H, CH₂), 1.68 (sextet 12H, ${}^{3}J_{\rm H-H} = 7.3$ Hz, CH₂), 1.52-1.47 (br, 16H, CH₂), 1.43–1.35 (br, 16H, CH₂), 1.11 (t, 18H, ${}^{3}J_{H-H} = 7.3$ Hz, CH₃), 1.02 (t, 18H, ${}^{3}J_{H-H} = 7.3$ Hz, CH₃), 0.93 (t, 12H, ${}^{3}J_{H-H} = 7.3$ Hz, CH₃), 0.92 (t, 12H, ${}^{3}J_{H-H} = 7.3$ Hz, CH₃). 0.41 (s, 9H, Si(CH₃)₃).

Trans-[5-(4-ethynylphenyl)-15-[trans-bis(1,4-ethynylphenyl)bis(tri-n-butyl-phosphine)-platinum(II)]-3,7,13,17-tetramethyl-2,8,12,18-tetrakis-(n-hexyl)-zinc(II)-porphyrin]-[5,15-bis(4-eth ynylphenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetrakis-(n-hexyl) $zinc(\Pi)$ -porphyrin]-bis(tri-n-butylphosphine)-platinum(Π) (8b). The porphyrin 8a (15.9 mg, 4.81 µmol) was dissolved in a mixture of tetrahydrofuran and dichloromethane (4.0 mL, 1:1 v/v). NBu₄F (40.0 µL, 1.0 M in THF) was added and the mixture was stirred at room temperature for 2 h. The solvent was removed in vacuo. The resulting red solid was recrystallized (CH₂Cl₂-CH₃OH). The red solid was washed with CH₃OH and collected with CH2Cl2. The solvent was removed in vacuo and the red solid was recrystallized a second time to afford the title compound 8b as a red solid in 98% yield (15.2 mg, 4.70 μ mol). HR-MS (MALDI-TOF): m/z = 3225.7667 $[M]^{+\bullet}$ 3225.7576 calcd for $C_{184}H_{262}N_8P_4Pt_2Zn_2$. This intermediate was not further characterized and was used directly in the following coupling step.

5,15-Bis[*trans*-(4-Ethynylphenyl)-[5-(4-ethynylphenyl)-15-[4-(trimethylsilyl)-ethynylphenyl]-3,7,13,17-tetramethyl-2,8,12,18tetrakis(n-hexyl)-zinc(II)-porphyrin]-bis-(tri-n-butylphosphine)platinum(II)]-3,7,13,17-tetramethyl-2,8,12,18-tetrahexyl-Zinc(II)porphyrin (7a). A mixture of porphyrin 3a (35.9 mg, 21.5 μ mol), and CuI (1.0 mg, 5.3 μ mol) was dissolved in CH₂Cl₂/Et₂NH (10 mL, 1:1 v/v). The porphyrin 1b (8.1 mg, 8.4 μ mol) was

solubilized in CH₂Cl₂ (10 mL) to be added over 1 h at room temperature with a dropping funnel. The mixture was stirred for an additional 1 h. After removal of the solvent in vacuo, the resulting mixture was purified by silica gel chromatography (20:60-30-60 CH₂Cl₂-pentane) with 0.5% Et₃N to afford 7a as a red solid in 20% yield (7.0 mg, 1.7 µmol). HR-MS (MALDI-TOF): $m/z = 4232.3957 \text{ [M]}^{+\bullet} 4232.3259$ calcd for $C_{246}H_{348}N_{12}P_4Pt_2Si_2Zn_3$. ³¹P NMR (161.92 MHz, CHCl₃) δ (ppm): 4.39. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 10.20 (s, 6H, H-meso), 8.05 (d, 4H, ${}^{3}J_{H-H} = 8.0$ Hz, Ph), 7.95–7.90 (m, 8H, Ph), 7.88 (d, 4H, ${}^{3}J_{H-H} = 8.0$ Hz, Ph), 7.71 (d, 8H, ${}^{3}J_{\rm H-H} = 8.0$ Hz, Ph), 4.04–3.92 (br, 24H, CH₂), 2.59 (s, 12H, CH₃), 2.58 (s, 12H, CH₃), 2.49 (s, 12H, CH₃), 2.48-2.40 (br, 24H, CH₂), 2.24-2.12 (br, 24H, CH₂), 1.93-1.82 (br, 24H, CH₂), 1.81–1.71 (br, 24H, CH₂), 1.68 (sextet, 24H, ${}^{3}J_{H-H} =$ 7.3 Hz, CH₂), 1.52-1.45 (br, 24H, CH₂), 1.44-1.35 (br, 24H, CH₂), 1.12 (t, 36H, ${}^{3}J_{H-H} = 7.3$ Hz, CH₃), 0.92 (m, 36H, CH₃), 0.41 (s, 18H, Si(CH₃)₃).

5,15-Bis[trans-(4-Ethynylphenyl)-[5,15-Bis(4-ethynylphenyl)-3,7,13,17-tetra-methyl-2,8,12,18-tetrakis(n-hexyl)zinc(II)porphyrin]-bis(tri-n-butylphosphine)-platinum(II)]-3,7,13,17-tetramethyl-2,8,12,18-tetrahexyl-Zinc(II)porphyrin (7b). The porphyrin 7a (6.0 mg, 1.4 µmol) was dissolved in tetrahydrofuran (2.0 mL). NBu₄F (10.0 µL, 1.0 M in THF) was added and the mixture was stirred at room temperature for 20 min. The solvent was removed in vacuo. The residue was recrystallized (CH₂Cl₂-CH₃OH). The red solid was washed with CH₃OH and collected with CH2Cl2. The solvent was removed in vacuo and the solid was recrystallized a second time to afford red the title compound 7a as a red solid in 78% yield (4.5 mg, µmol). HR-MS (MALDI-TOF): m/z = 4088.21381.1 $[M]^{+\bullet}$ 4088.2468 calcd for C₂₄₀H₃₃₂N₁₂P₄Pt₂Zn₃. ³¹P NMR (161.92 MHz, CHCl₃) δ (ppm): 4.39. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 10.20 (s, 6H, H-meso), 8.08 (d, 4H, ${}^{3}J_{H-H} =$ 8.0 Hz, Ph), 7.95–7.86 (m, 12H, Ph), 7.71 (d, 8H, ${}^{3}J_{H-H} = 8.0$ Hz, Ph), 4.03-3.83 (br, 24H, CH₂), 3.34 (s, 2H, CH), 2.59 (s, 12H, CH₃), 2.58 (s, 12H, CH₃), 2.49 (s, 12H, CH₃), 2.48–2.42 (br, 24H, CH₂), 2.24–2.16 (br, 24H, CH₂), 1.94–1.84 (br, 24H, CH₂), 1.81-1.72 (br, 24H, CH₂), 1.72-1.62 (br, 24H, CH₂), 1.55-1.46 (br, 24H, CH₂), 1.45–1.38 (m, 24H, CH₂), 1.12 (t, 36H, ${}^{3}J_{H-H} = 7.3$ Hz, CH₃), 0.97–0.89 (m, 36H, CH₃).

5,15-Bis[trans-(4-Ethynylphenyl)-[5-(4-ethynylphenyl)-15-[transbis(1.4-ethynylphenyl)-bis(tri-n-butylphosphine)-platinum(II)l-3,7,13,17-tetramethyl-2,8,12,18-tetrakis-(n-hexyl)-zinc(II)-porphyrin|bis(tri-n-butylphosphine)-platinum(II)]-3,7,13, 17-tetramethyl-2,8,12,18-tetrahexyl-Zinc(II)porphyrin (9). A mixture of the porphyrin 7b (1.4 mg, 0.34 µmol), trans-phenylethynylchlorobis(tri-n-butylphosphine)platinum(II) (1.0 mg, 1.4 µmol) and CuCl (0.2 mg, 2 µmol) was dissolved in CH2Cl2/Et2NH (1.0 mL, 1:1 v/v). The solution was stirred at room temperature for 30 min. After removal of the solvent in vacuo, the residue was recrystallized (CH2Cl2-CH3OH). The red solid was washed with CH₃OH and collected with CH₂Cl₂. The solvent was evaporated in vacuo and the red solid was recrystallized a second time to afford 9 as a red solid in 53% yield (1.0 mg, 0.18 µmol). HR-MS (MALDI-TOF): $m/z = 5487.1266 \text{ [M]}^{+\bullet} 5486.9791$ calcd for $C_{304}H_{448}N_{12}P_8Pt_4Zn_3$.

Trans-bis[trans-[5,15-bis(4-ethynylphenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetrakis(n-hexyl)zinc(II)porphyrin]-[5-(4-ethynylphenyl)-15-[4-(trimethylsilyl)-ethynylphenyl]-3,7,13,17-tetramethyl-2,8,12,18-tetrakis(n-hexyl)-zinc(II)-porphyrin|-bis-(trin-butylphosphine)-platinum(II)l-bis-(tri-n-butylphosphine)platinum(II) (10a). A mixture of porphyrin 3a (21.0 mg, 12.6 µmol), porphyrin 5b (11.3 mg, 4.46 µmol) and CuCl (0.5 mg, 5.1 µmol) was dissolved in CH₂Cl₂/Et₂NH (5.0 mL, 1:1 v/v). The solution was stirred at room temperature for 30 min. After removal of the solvent in vacuo, the resulting mixture was recrystallized (CH₂Cl₂-CH₃OH). The red solid was washed with CH₃OH and collected with CH₂Cl₂. The solvent was evaporated in vacuo and the red solid was recrystallized a second time to afford 10a as a red solid in 98% yield (25.5 mg, 4.40 μ mol). HR-MS (MALDI-TOF): m/z =5795.2374 $[M]^{+}$ 5794.1812 calcd for C₃₃₄H₄₇₆N₁₆P₆Pt₃Si₂Zn₄. ³¹P NMR (161.92 MHz, CHCl₃) δ (ppm): 4.41. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 10.20 (s, 4H, H-meso), 10.19 (s, 4H, H-meso), 8.05 (d, 4H, ${}^{3}J_{H-H} = 8.0$ Hz, Ph), 7.95–7.91 (m, 12H, Ph), 7.88 (d, 4H, ${}^{3}J_{H-H} = 8.0$ Hz, Ph), 7.71 (d, 12H, ${}^{3}J_{\rm H-H} = 8.0$ Hz, Ph), 4.05–3.91 (br, 32H, CH₂), 2.59 (s, 24H, CH₃), 2.58 (s, 12H, CH₃), 2.48 (s, 12H, CH₃), 2.47-2.42 (br, 36H, CH₂), 2.25–2.14 (br, 32H, CH₂), 1.95–1.84 (br, 36H, CH₂), 1.82–1.64 (m, 68H, CH₂), 1.56–1.46 (br, 32H, CH₂), 1.46–1.35 (br, 32H, CH₂), 1.12 (t, 54H, ${}^{3}J_{H-H} = 7.3$ Hz, CH₃), 0.98-0.90 (m, 48H, CH₃), 0.41 (s, 18H, Si(CH₃)₃).

Trans-bisltrans-bisl5.15-bis(4-ethynylphenyl)-3.7.13.17-tetramethyl-2,8,12,18-tetrakis(n-hexyl)zinc(II)porphyrin]-3,7,13,17tetramethyl-2,8,12,18-tetrakis(n-hexyl)-zinc(II)-porphyrin]-bis (tri-n-butylphosphine)platinum(II)]-bis(tri-n-butylphosphine)platinum(II) (10b). The porphyrin 10a (6.0 mg, 1.0 μ mol) was dissolved in tetrahydrofuran (1.0 mL). NBu₄F (1.0 M in THF) was added and the mixture was stirred at room temperature for 30 min. The solvent was removed in vacuo. The residue was recrystallized (CH₂Cl₂-CH₃OH). The red solid was washed with CH₃OH and collected with CH₂Cl₂. The solvent was removed in vacuo and the red solid was recrystallized a second time to afford the title compound 10b as a red solid in 83% yield (4.8 mg, 0.85 μ mol). HR-MS (MALDI-TOF): m/z = 5650.2302 $[M]^{+\bullet}$ 5650.1022 calcd for $C_{328}H_{460}N_{16}P_6Pt_3Zn_4$. ³¹P NMR (161.92 MHz, CHCl₃) δ (ppm): 4.39. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 10.20 (s, 8H, H-meso), 8.08 (d, 4H, ${}^{3}J_{H-H} =$ 8.0 Hz, Ph), 7.96–7.87 (m, 16H, Ph), 7.71 (d, 12H, ${}^{3}J_{H-H} =$ 8.0 Hz, Ph), 4.05-3.92 (br, 32H, CH₂), 3.34 (s, 2H, CH), 2.58 (s, 36H, CH₃), 2.49 (s, 12H, CH₃), 2.47-2.41 (br, 36H, CH₂), 2.25-2.14 (br, 32H, CH₂), 1.95-1.82 (br, 36H, CH₂), 1.81-1.63 (br, 68H, CH₂), 1.52-1.46 (br, 32H, CH₂), 1.45-1.35 (br, 32H, CH₂), 1.12 (t, 54H, ${}^{3}J_{H-H} = 7.3$ Hz, CH₃), 0.98–0.89 (m, 48H, CH3).

Trans-bis[*trans*-[5,15-bis(4-ethynylphenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetrakis(n-hexyl)zinc(π)porphyrin]-[5-(4ethynylphenyl)-15-[*trans*-bis(1,4-ethynylphenyl)-bis(tri-n-butylphosphine)-platinum(π)]-3,7,13,17-tetramethyl-2,8,12,18-tetrakis-(n-hexyl)-zinc(π)porphyrin]-bis(tri-n-butylphosphine)platinum(π)]bis(tri-n-butylphosphine)platinum(π) (11). A mixture of the porphyrin 10b (4.0 mg, 0.71 µmol), *trans*-phenylethynylchloro-bis(tri-n-butylphosphine)platinum(π) (3.2 mg, 4.3 µmol)

and CuCl (0.5 mg, 5 µmol) was dissolved in CH₂Cl₂/Et₂NH (2.0 mL, 1:1 v/v). The solution was stirred at room temperature for 30 min. After removal of the solvent in vacuo, the residue was recrystallized (CH₂Cl₂-CH₃OH). The red solid was washed with CH₃OH and collected with CH₂Cl₂. The solvent was evaporated in vacuo and the red solid was recrystallized a second time to afford 11 as a red solid in 82% yield (4.1 mg, 5.8 μ mol). MS (MALDI-TOF): m/z = 7060.4221 $[M]^{+}$ 7059.6427 calcd for $C_{392}H_{576}N_{16}P_{10}Pt_5Zn_4$ (average mass). ³¹P NMR (161.92 MHz, CHCl₃) δ (ppm): 4.39, 4.27. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 10.21 (s, 4H, H-meso), 10.19 (s, 4H, H-meso), 7.96-7.87 (d, 12H, Ph), 7.71 (d, 16H, ${}^{3}J_{H-H} = 8.0$ Hz, Ph), 7.65 (d. 4H, ${}^{3}J_{H-H} = 8.0$ Hz, Ph), 8.0 (d. 4H, ${}^{3}J_{H-H} = 8.0$ Hz, Ph),7.24 (d. 6H, ${}^{3}J_{H-H} = 8.0$ Hz, Ph), 4.05-3.92 (br, 32H, CH₂), 2.59 (s, 24H, CH₃), 2.58 (s, 12H, CH₃), 2.55 (s, 12H, CH₃), 2.49–2.41 (br, 36H, CH₂), 2.25–2.14 (br, 32H, CH₂), 1.95–1.82 (br, 36H, CH₂), 1.81–1.63 (m, 116H, CH₂), 1.61–1.46 (m, 56H, CH₂), 1.45-1.35 (br, 32H, CH₂), 1.12 (t, 54H, ${}^{3}J_{H-H} = 7.3$ Hz, CH₃), 1.02 (t, 36H, ${}^{3}J_{H-H} = 7.3$ Hz, CH₃), 0.98–0.89 (m, 48H, CH₃).

Instruments

¹H NMR spectra were recorded on a Bruker DRX 300 MHz AVANCE spectrometer at the "Plateforme d'Analyse Chimique et de Synthèse Moléculaire de l'Université de Bourgogne (PACS-MUB)" or on a Bruker AVANCE III 400 MHz spectrometer (¹H 400.13 MHz and ³¹P 161.92 MHz) using the solvent as a chemical shift standard, except for the ³¹P NMR, where the chemical shifts are relative to H₃PO₄ 85% in D₂O. All chemical shifts (δ) and coupling constants (J) are given in ppm and Hertz, respectively. The spectra were measured from freshly prepared samples in chloroform. The mass spectra were obtained on a Bruker Daltonics Ultraflex II spectrometer at the PACSMUB in the MALDI/TOF reflectron mode using dithranol as a matrix. High resolution mass measurements (HR-MS) were carried out in the same conditions as previously using PEG ion series as internal calibrant. The UV-visible spectra were recorded on a Varian Cary 1 spectrophotometer or on a Hewlett-Packard diode array model 8452A. UV-visible spectra were recorded on a Hewlett-Packard diode array model 8452A and the emission spectra were obtained using a double monochromator Fluorolog 2 instrument from Spex. The emission lifetimes were measured using a TimeMaster Model TM-3/2003 apparatus from PTI. The source was nitrogen laser with high-resolution dye laser (fwhm ~ 1600 ps) and the emission lifetimes were obtained from deconvolution of decay curves monitored at three different emission wavelengths. The uncertainties in the lifetimes were about 10-50 ps based on multiple measurements.

Quantum yields

The quantum yields measurements were performed in 2MeTHF at 298 K using Zn(TPP) (TPP = tetraphenylporphyrin; $\Phi = 0.033$)³⁰ as a reference. The solutions for the samples and the reference were prepared under inert atmosphere (in a glove box, $P_{O_2} < 50$ ppm). Solutions prepared for both the reference and the samples were adjusted to obtain absorbencies in the range of 0.02–0.05 where three different solutions for each measurement were used. The absorbance was adjusted to be the same as much as possible for the standard and the sample for each measurement.

Results and discussion

Syntheses and characterization

The structures of the Pt(bisethynyl)/Zn(porphyrin) oligomers are shown in Chart 2 and 3. The symmetrical porphyrin precursor **1a** was prepared as described in the literature (Scheme 1).^{28,29} The subsequent elimination of the two







trimethylsilyl groups with TBAF/THF produced the corresponding diethynyl porphyrin **1b** in 94% yield (Scheme 2).

A general procedure to synthesize monomeric or oligomeric compounds could involved e.g. a dehydrohalogenation reaction between the trans-Pt(PBu₃)₂Cl₂ and the appropriate ethynylporphyrin in a dichloromethane/diethylamine mixture (1:1 v/v), at room temperature in the presence of CuX (X = Cl, I).³¹ The mechanism is analog to a Sonogashira coupling.^{32,33} It is worth noting that copper chloride can be preferred to copper iodide¹³ as, in some cases, the yields of the coupling reactions were higher and the formation of polar by-products was decreased. This coupling strategy was first used to access to the porphyrin dimer **5b** as described in Scheme 2. Indeed, reaction of the symmetrical diethynyl porphyrin 1b with transdichlorobis(tri-n-butylphosphine)platinum(II) under N2 and in the presence of CuI leads to the formation of the expected porphyrin dimer 5b (as monitored by MALDI/TOF mass spectrometry). Unfortunately, due to a low selectivity, the presence of different porphyrin oligomers (trimers, tetramers,...) was also observed by MALDI/TOF mass spectrometry (Fig. S1) and TLC. Indeed, the main downfall of this first approach is that the reaction is quite uncontrolled resulting in a complex mixture of oligomers with different chain lengths (Fig. S1). Laborious and lengthy chromatographic separations were attempted affording only small quantities of the desired porphyrin dimer 5b. Therefore, this way was not further considered.

This latter result led us to investigate a new one-step procedure to synthesize porphyrins **5a** and **5b**. Indeed, the other possible route to obtain the porphyrin **5a** and to avoid further oligomerization, consists in the coupling reaction of the unsymmetrical monoethynyl porphyrin **1c** (prepared as described in Scheme 3) with *trans*-dichlorobis(tri-n-butylphosphine)platinum(II). This key intermediate was successfully prepared by using only one equivalent of K_2CO_3 during the deprotection step. The generation of the latter product was monitored by MALDI/TOF mass spectrometry until



maximization of the experimental conditions. The unreacted symmetrical porphyrin precursor **1a** did not affect any further coupling reaction and was recovered afterwards. The synthetic procedure (Scheme 3) was successfully performed by reacting *trans*-dichlorobis(tri-n-butylphosphine)platinum(II) with **1c** under the same coupling reaction conditions as indicated above in Scheme 2. Porphyrin dimer **5a** was obtained in a quantitative yield (Scheme 4). The subsequent deprotection of the trimethyl silyl group by K_2CO_3 easily led to **5b** in almost quantitative yield.

The synthetic pathway leading to the porphyrin tetramer is shown in Scheme 3. The key unsymmetrical monoethynyl porphyrin 1c was used for this synthesis. The synthetic route to porphyrin tetramer 11 requires first the preparation of the monoethynyl dimer 8a as successfully performed. Porphyrins 2a and 3a were easily prepared in high yields by coupling, in the presence of CuI, porphyrin 1c with *trans*-phenylethynylchlorobis(tri-n-butylphosphine)platinum(II) and *trans*-bis(trin-butylphosphine)-dichloroplatinum(II), respectively. In both cases, these coupling reactions were monitored by TLC and MALDI/TOF mass spectrometry. The subsequent reaction of porphyrin dimer 8a with *trans*-Pt(PBu₃)₂Cl₂ afforded the desired tetramer 11 in 30% yield.

The preparation of the porphyrin tetramer 11 was further improved through the reaction of the symmetrical dimer 5awith porphyrin 3a using the same coupling conditions as employed for 6 (Scheme 4) with, in this case, CuI being replaced by CuCl. It is worth noting that the synthetic strategy applied to the synthesis of oligomers containing an even number of porphyrin units (*e.g.* porphyrin dimers, tetramers) could also be applied to the preparation of oligomers containing an odd number of porphyrin units (*e.g.* porphyrin trimers) as described in Scheme 5. This was successfully performed by reacting the diethynyl porphyrin 1b with porphyrin 3a under the same coupling conditions as above (Scheme 5) leading to 7a and 9 in very good yields.

The main advantage of this synthetic method is the stepby-step control of the oligomers length coupled by a high solubility due, mainly, to the presence of four long-chain n-hexyl substituents at the β -positions of the porphyrin







macrocycles. The reported products in this work exhibit good solubility in common solvent.

All the compounds were fully characterized by spectroscopic methods. The NMR (¹H, and ³¹P), and mass spectral data shown in the Experimental Section are consistent with their chemical structures.

Absorption and emission spectroscopy

In order to analyze the excited state behavior of the oligomers, the representative model complexes 4, 6, and 11 were investigated by means of absorption and emission spectroscopy. During the course of this investigation, the possibility of aggregation was also considered. Indeed, compounds of the type *trans*-ArC \equiv C-PtL₂-C \equiv CAr (even where L = PBu₃) are known to form aggregates at high concentrations which modify the spectral signatures and excited state dynamics.³⁴ But upon adding bulky groups, such as dendrons for examples, this aggregation phenomenon has not been observed.³⁵ We also observed the same phenomenon (*i.e.* non-aggregation in oligomers, polymers and model compounds with other bulky substituents),^{35,36} even for species containing zinc(II) porphyrin units well known for forming J-and H-aggregates.^{10,11} In this work, the spectra and dynamics were found concentration independent in the range investigated (typically 10^{-6} to 10^{-5} M).

The examination of the absorption spectra was first made at room temperature (Fig. 1 and Table 1). The spectra are typical from other porphyrin compounds. The existence of exciton couplings denoted as a shoulder on the high energy side of the Soret band for 6, 9 and 11 at room temperature but not for





Fig. 1 UV-vis spectra of **4** (dotted line) and **11** (straight line) in toluene at 298 K stressing the exciton coupling.

4 when using 2MeTHF as the solvent (Table 2). In order to confirm the presence of a spectral feature, the 77 K spectra of 4, 6 and 11 were also measured (Fig. 2). At this temperature, the shoulder is well resolved into a peak allowing one to measure accurately this constant. Again, this high energy peak is absent in 4 supporting the exciton coupling assignment. A coupling constant of 400 cm^{-1} is observed for 11, which is weak, but not negligible. This observation appears unusual when one considers the size of the Pt-containing spacer $(H \cdots H)$ distance in *trans*-ArC \equiv C-PtL₂-C \equiv CAr (Ar = 2,5- $C_6Me_2H_3$ - and 3,5- $C_6Me_2H_3$) is ~18 Å.³⁷ The coupling constants increase as the number of units in the chain increases from 0 to 280 cm⁻¹ at 298 K or 405 cm⁻¹ at 77 K (Table 2). This observation, *i.e.* the presence of a long distance interaction is also consistent with the recent evidence for efficient singlet energy transfer in dyads built upon this rigid conjugated spacer of the type $M(\mathbf{P})-C_6H_4C \equiv C-PtL_2-C \equiv$ $CC_6H_4-M'(\mathbf{P})$ where M and M' are Pd (donor) or zinc (acceptor), L is PEt₃ and **P** is hexamethyldiethylporphyrin.²⁴

The photophysical parameters, fluorescence lifetimes (τ_F) and quantum yields (Φ_F) are placed in Table 3. The Φ_F data for **4**, **6** and **11** are constant, which is consistent with the lack

 $\lambda \text{ [nm]}(\epsilon \times 10^{-3} \text{ M}^{-1} \text{ cm}^{-1})$ Soret band O bands Compound Monomers 579 (4) 1b 416 (374) 545 (16) 2b 418 (520) 544 (12) 578 (5) 579 (2) 3b 418 (249) 545 (10) 578 (3) 4 420 (172) 546 (9) Dimers 5b 419 (519) 545 (20) 578 (6) 578 (7) 6 421 (498) 545 (28) 8b 420 (427) 544 (17) 579 (7) Trimers 7b 421 (254) 546 (15) 579 (5) 9 422 (243) 545 (12) 579 (3) Tetramers 10b 421 (250) 544 (16) 577 (5) 11 423 (532) 544 (27) 578 (6)

 Table 2 Exciton coupling constants (cm⁻¹)

Species	Constant (298 K)	Constant (77 K)		
Monomer 4 Dimer 6 Trimer 9	0 170 225	0 not measured 325		
Tetramer 11	280	405		

of conjugation along the oligomers; the chromophores act independently. Settle variations cannot be detected because of the uncertainties of the measurements ($\pm 10\%$). The possibility of exciton phenomenon^{38,39} in the excited states was tested.

The exciton phenomenon may manifest itself by exhibiting τ_F being fluorescence wavelength dependent.³⁸ This possibility was checked (Table 3). All decays turned out to be single exponential and no strong variation of the τ_F with the



Fig. 2 Absorption (solid), excitation (dotted . . .), and emission (broken - - -) of **4** (n = 1), **6** (n = 2) and **11** (n = 4) measured in 2MeTHF: (A) At 298 K where $\lambda_{em} = 505$ nm and $\lambda_{ex} = 640$ nm; (B) At 77 K where $\lambda_{em} = 535$ nm and $\lambda_{ex} = 635$ nm.

fluorescence wavelength was observed. This observation is totally consistent with the long distance between the chromophores (~18 Å). The other trend is the settle decrease in $\tau_{\rm F}$

going from the monomer 4 to dimer 6 and tetramer 11. Because the change is small, measurements were also repeated at 77 K. The τ_F data exhibit an increase upon cooling, which is

		$\tau_{\rm F}({\rm ns})$									
		298 K						77 K			
		$\lambda_{\rm mon} = 575 \ {\rm nm}^b$		$\lambda_{\rm mon} = 585 \ {\rm nm}^b$		$\lambda_{\rm mon} = 595 \ {\rm nm}^b$			$\lambda_{\rm mon} = 575 \ {\rm nm}^b$		
	${\Phi_{ m F}}^a$	χ^2	$\tau_{\rm F}$	χ^2	$\tau_{\rm F}$	χ^2	$\tau_{\rm F}$	τ_{Fav}	χ^2	$\tau_{\rm F}$	
4 6 11	0.021 0.021 0.021	0.99 0.71 1.15	$\begin{array}{c} 1.34 \pm 0.02 \\ 1.31 \pm 0.01 \\ 1.30 \pm 0.01 \end{array}$	1.02 1.32 0.91	$\begin{array}{c} 1.35 \pm 0.02 \\ 1.33 \pm 0.01 \\ 1.30 \pm 0.02 \end{array}$	1.08 0.79 0.77	$\begin{array}{c} 1.40 \pm 0.02 \\ 1.39 \pm 0.01 \\ 1.34 \pm 0.01 \end{array}$	$\begin{array}{c} 1.36 \pm 0.02 \\ 1.35 \pm 0.01 \\ 1.31 \pm 0.01 \end{array}$	0.97 1.14 0.92	$\begin{array}{c} 1.51 \pm 0.08 \\ 1.49 \pm 0.02 \\ 1.45 \pm 0.04 \end{array}$	

Table 3 Fluorescence lifetime and quantum yields

^{*a*} The quantum yields were measured using $\lambda_{exc} = 505$ nm and the uncertainties in the measured values were $\pm 10\%$ based on multiple measurements. ^{*b*} The emission wavelength at which the fluorescence lifetime was measured. The uncertainties are those extracted from the deconvolution data. ^{*c*} The wavelength corresponding to the first maximum fluorescence emission peak.

consistent with the increase in medium rigidity. The trend (a decrease in τ_F with the oligomer length) remains but this variation is very small. The proposed interpretation for this decrease in τ_F is a slight increase in internal conversion rate constant (k_{ic}) as the oligomer gets longer. This slight increase (rather than a large one) is consistent with the "rigid stick" nature of the oligomers.

In order to corroborate this hypothesis, the phosphorescence spectra of monomer **4** to dimer **6** and tetramer **11** were examined (Fig. 3). Because both τ_F and Φ_F are relatively constant at 298 K, and the τ_F data at 77 K also according to the data listed in Table 3, it is reasonably assumed that the Φ_F data at 77 K is also relatively constant as well. The phosphorescence bands for these oligomers are depicted in the 700–850 nm range (Fig. 3), where it is normally expected.^{25,26} The relative intensity of the phosphorescence band *vs.* the fluorescence decreases with the oligomer length by at least a factor of 2. This is indicative that the internal conversion rate constant from the triplet state, k_{ip} , must unavoidably increase along this series. The phosphorescence lifetimes, τ_P , were not measured in this work.

Conclusion

We reported a methodology that gives easy access to monodispersed oligomers. The key features is that (1) one prepares end groups such as the trans-C₆H₅C = CPt(PBu₃)₂Cl unit (hence providing an unfunctionalizable end group (Ph)), (2) incorporates soluble groups such a hexyls, (3) controls the combination of the Pt-Cl units (as end group or trans-PtCl₂(PBu₃)₂) with the bis(ethynyl)porphyrins via the use of relative but strategic amounts, and importantly (4) controls the deprotection of the bis(ethynylsilane)porphyrin precursor to form the very convenient mono(ethynyl)mono(ethynylsilane)porphyrin derivative. Just as proof of concept, the monomer, dimer, trimer and tetramers were prepared in this work, and the good solubility of the resulting targets suggest that larger oligomers could be obtained. However, the preparation of very long oligomers was not the goal of this work. Evidence for excitonic coupling was made, but such interactions turned out to be relatively weak. The photophysical parameters, notably $\tau_{\rm F}$ and $\Phi_{\rm F}$, are relatively constant but a small decrease in lifetimes suggest that k_{ic} must increase slightly as the oligomer gets longer. All in all, this paper reports the synthetic strategy to obtained well defined oligomers of Pt(bisethynyl)/ Zn(porphyrin) systems. Future work involves the rational synthesis of the conjugated analogues, by removing the substituents placed at the β -positions, and perform a comparative study.

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