

Symmetric, twinned, and double-decker phthalocyanines substituted by trialkylated pentaerythritol

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Trialkylated pentaerythritol was chosen as a bulky substituent for a set of 3 free-base phthalocyanines: a symmetric, a twinned, and a double-decker derivative. The bulkiness of this substituent lowered the aggregation of the phthalocyanines. The electronic absorptions were comparatively investigated: the twinned phthalocyanine exhibited a significant near-infrared shifted absorption. The neutral radical Eu(III) complex was oxidized by bromine. These 3 phthalocyanines are promising for use as molecular materials.

Key Words: Phthalocyanine, twinned, alkylated pentaerythritol, europium, double-decker, electronic near-infrared delocalization

Introduction

Phthalocyanines, also named tetrabenzotetraazaporphyrins, are tetrapyrrolic derivatives with a delocalized 18 π electronic structure, thus exhibiting original spectroscopic, photophysical, photochemical, and electronic properties, including a near-infrared absorption centered generally at 680 nm but extendable up to 1000 nm by extending the electronic delocalization.¹ The unique structure of phthalocyanines offers several possibilities for such modulations: the substitution pattern (nature, number, and position of the substituents) and the metallation pattern (with possible axial substitution depending on the nature of the metal).

These properties are suitable in molecular materials for various applications emerging in recent years:² phthalocyanines are extensively used as sensors,^{3–5} photosensitizers for photodynamic therapy⁶ and photocatalysis,⁷ oxidation catalysts,^{8,9} or materials exhibiting non-linear properties.^{10,11} Many of the required properties can be enhanced and tailored by an extension of electronic delocalization. Several twinned phthalocyanines have

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been reported to date, joined by one or more benzene ring.^{1,12–20} The effect of the electronic delocalization on a near-infrared (NIR) shifted maximum absorption was demonstrated by a comparison with a twinned phthalocyanine in which the joining unit does not allow the conjugation over the 2 phthalocyanine rings.²¹ Naphthalocyanines²² and related tetraimidazophthalocyanines²³ exhibit similar NIR shifted absorption. The formation of bisphthalocyanines, or double-deckers, is another way to extend the range of possible applications.

One of the main drawbacks of phthalocyanines is their aggregation tendencies. Substituting phthalocyanines with bulky substituents is a preeminent strategy developed to limit aggregation. *tert*-Butylphthalonitrile is even a commercial compound. *tert*-Butyl substitution has some limits in the case of *tert*-butylsulfanyl substitution, as it has a tendency to stick anyway to columns and limits purification possibilities, especially in the case of asymmetrically substituted derivatives.^{24–26} The size of substituents is likely to have an effect even on the metal oxidation state of N-bridged phthalocyanines.²⁷ The position of substituents is another important factor: non-peripheral substituents, as they prevent macrocycles coming to close to each other, inhibit aggregation as well.²⁸ This is particularly important for photosensitizers at avoiding the quenching of the electronic events leading to the formation of singlet oxygen.^{28–30} The addition of dissociating agents such as Triton-X100 is another option.

Trialkylated pentaerythritol substituent appeared to be particularly adequate to avoid or lower aggregation. The presence of 3 alkyl chains on a tertiary carbon is likely to enhance the solubility of the phthalocyanines and to reduce even more their aggregation.

We therefore decided to substitute 3 phthalocyanine derivatives with trialkylated pentaerythritol and designed the symmetrically substituted monomeric derivative (**1**), the twinned phthalocyanine (**2**) having 2 phthalocyanine macrocycles united by a single benzene ring, and the europium (III) double-decker (**3**). The structures of these 3 targeted phthalocyanines are represented in Figure 1.

Results and discussion

Syntheses and characterizations

Phthalonitrile (**7**) is the key precursor of the synthesis of the 3 targeted phthalocyanines. Its synthesis is represented in Scheme 1.

Tri-O-hexyl pentaerythritol (**5**) was prepared from pentaerythritol in phase transfer catalysis conditions as previously described by us (**4**).³¹ It was then used as a nucleophile in the nitro substitution achieved on 4-nitrophthalonitrile (**6**), a widely used reaction. The substitution was performed in standard conditions: 60 °C in DMF, in the presence of potassium carbonate. Two equivalents of **1** were employed: the steric hindrance of tri-O-hexyl pentaerythritol (**5**) slows the reaction compared to the case of a less hindered alcohol. The structure of phthalonitrile (**7**) was fully confirmed by the analyses performed. The ESI spectrum shows the molecular adduct of Na as well as the 2M+Na peak, both fitting the theoretical pattern (Figure 2). ¹H- and ¹³C-NMR and IR are in accordance with the proposed structure.

Phthalonitrile (**7**) was cyclotetramerized in lithium templating conditions. This was followed by the lithium removal and led to phthalocyanine **1** in excellent yield (58%). Twinned phthalocyanine (**2**) was prepared by a mixed condensation of bisdiiminoisoindoline (**8**)¹⁷ with a 15-fold of phthalonitrile (**7**), also in lithium

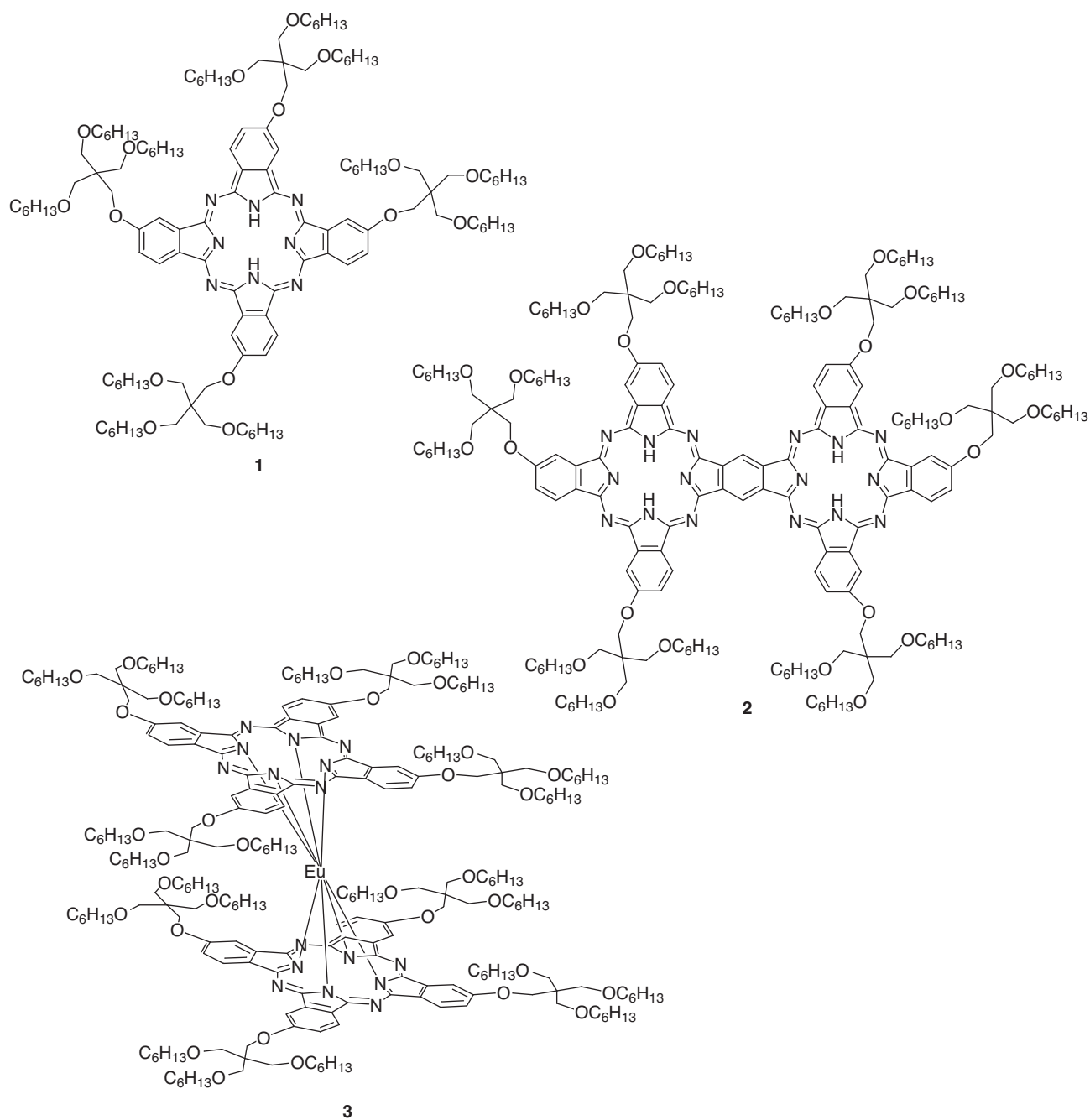
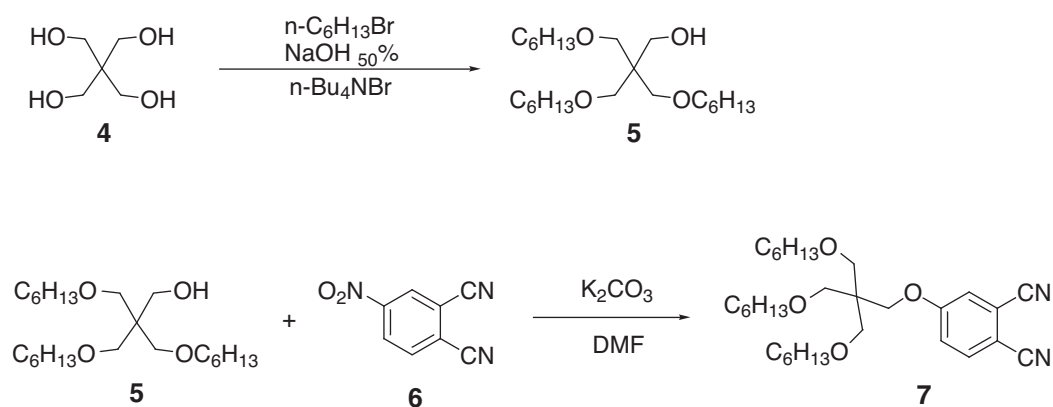


Figure 1. Structures of trialkylated pentaerythritol substituted monomeric phthalocyanine (**1**), of twinned phthalocyanine (**2**), and of europium (III) double-decker (**3**). Only one of the possible isomers is represented.

templating conditions (Scheme 2). The strong excess of phthalonitrile (**7**) aims to avoid the self-condensation of the bisdiiminoisoindoline leading to undesired polymeric by-products. Only 2 major compounds are indeed obtained: the symmetric derivative **1** and the desired phthalocyanine **2** (8%). This yield is quite good as the



Scheme 1. Synthesis of the precursor phthalonitrile **7**.

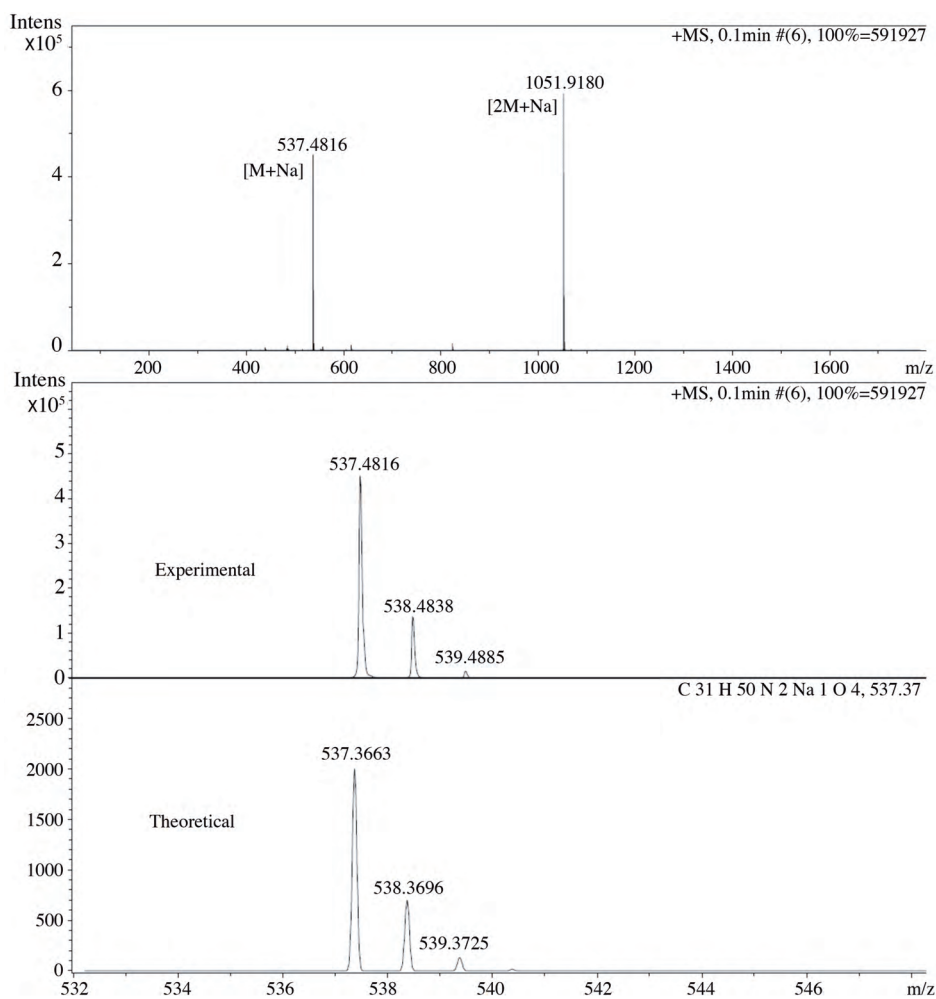


Figure 2. Theoretical and experimental ESI spectra of phthalonitrile **7**.

formation of a twinned phthalocyanine can be considered as the double formation of AB3-type derivative, a reaction that we usually perform in 15%-20% yield.³²⁻³⁴ The MALDI spectrum of the clean mixture of these 2 phthalocyanines is represented in Figure 3. This mixture is then separated by gel-permeation chromatography (Biobeads). Analyses are in accordance with the proposed structure.

Europium double-decker complex **3** (Figure 1) was prepared from **1**, using $\text{Eu}(\text{OAc})_3$ as the metal salt, in 1-chloronaphthalene and DBU. Due to the steric hindrance of the substituents likely to prevent the required proximity of 2 macrocycles to form the double-decker complex, the obtained 32% yield is quite satisfactory.

Electronic absorption properties

The maximum absorption wavelengths and related extinction coefficient of **1** and **2** are summarized in the Table. Related spectra are presented in Figure 4. The spectrum of **1** is typical of a free-base phthalocyanine: the absence of a coordinating metal at the center of the phthalocyanine induces a loss of symmetry, which results in a characteristic split Q band. A NIR shift of roughly 140 nm compared to **1** is induced by the electronic delocalization over the 2 phthalocyanine macrocycles. Remaining aggregation enlarges the Q band of the twinned phthalocyanine **2**, but the splitting of the Q band is visible both on the monomeric and on the aggregated form of the phthalocyanine.

The UV-Vis spectra of the double-decker europium complex **3** under its neutral radical form and of the oxidized form are presented in Figure 5. The neutral complex (**3**) is oxidized using a solution of Br_2 in CHCl_3 . The characteristic band corresponding to the radical absorption centered at 1750 nm disappears with the addition of bromine and the subsequent oxidation of the complex. This is consistent with our previous observations.^{35,3}

Table. UV-Vis data of compounds **1** and **2**.

Compound	Solvent	λ_{max} nm (log ϵ)
1	THF	704 (5.25)
		666 (5.17)
		344 (4.96)
	CHCl_3	707 (4.76)
		670 (4.68)
		344 (4.48)
2	THF	845 (4.05)
		780 (3.28)
		690 (4.60)
		344 (4.58)
	CHCl_3	845 (4.27)
		780 (4.32)
		690 (4.67)
		344 (4.84)

Experimental

Materials and methods

All reaction solvents were dried and purified as described by Perrin and Armarego.³⁷ Optical spectra in the UV-visible region were recorded with a Shimadzu 2001 UV spectrophotometer using a 1 cm path length cuvette at room temperature. The mass spectra were recorded on a LCQ-ion trap (Thermo Finnigan, San Jose, CA, USA), equipped with an electrospray source and matrix assisted laser desorption ionization BRUKER Microflex LT using 2,5-dihydroxybenzoic acid (DHB) as matrix. ¹H- and ¹³C-NMR spectra were recorded in CDCl₃ solutions on a Varian 500 MHz spectrometer. IR spectrum was recorded between 4000 and 650 cm⁻¹ using a Perkin Elmer Spectrum 100 FT-IR spectrometer with an attenuated total reflection (ATR) accessory featuring a zinc selenide (ZnSe) crystal.

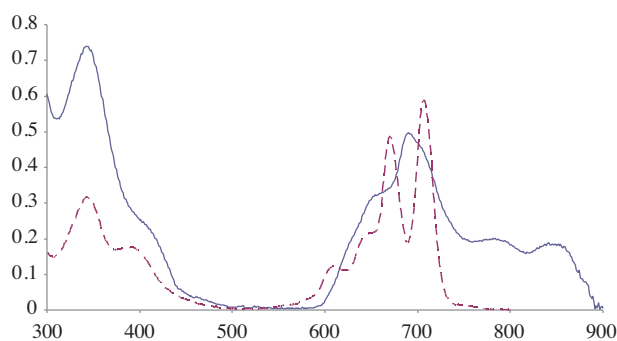


Figure 4. UV-Vis spectra of **1** (discontinued line) and **2** (continued line) in chloroform. Concentration 10 μ M.

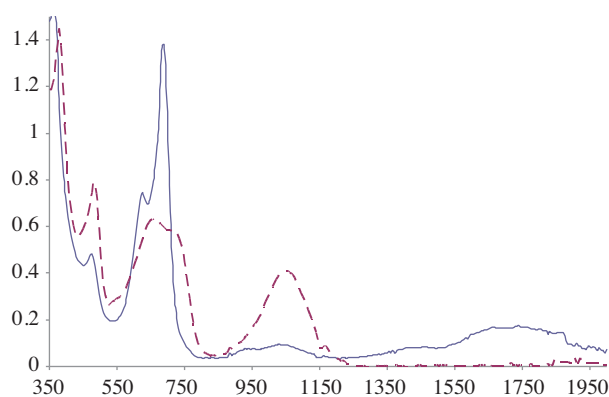


Figure 5. UV-Vis spectra of **3**: neutral radical form (continued line) and oxidized form (discontinued line) in chloroform. Concentration 20 μ M.

Syntheses

Phthalonitrile (7). Trialkylated pentaerythritol (**5**)³¹ (2.5 g, 6.44 mmol), 4-nitrophthalonitrile (**6**) (560 mg, 3.22 mmol) and potassium carbonate (9 g, 65 mmol) were stirred for 3 days in DMF (20 mL) at 60 °C. The cooled reaction mixture was diluted with dichloromethane (200 mL), washed with water (3 \times 200 mL), dried on sodium sulfate, and concentrated. The expected phthalonitrile was then purified by silica gel column chromatography, yielding a transparent oil. 2.1 g, 60%. C₃₁H₅₀N₂O₄. MW 514.74. ¹H-NMR (500 MHz, CDCl₃, δ , ppm): 7.31, 7.22, 7.20 (3H, aromatics), 4.08 (s, 2H, C_{Ar}OC_H₂C), 3.46 (s, 6H, CCH₂OC₆H₁₃), 3.37 (t, 6H, -OC_H₂C₅H₁₁), 1.52 (m, 6H, -CH₂C₄H₉), 1.28 (m, 18H, -(CH₂)₃CH₃), 0.89 (s, 9H, -CH₃). ¹³C-NMR (126 MHz, CDCl₃, δ , ppm): 162.88, 135.30, 120.00, 119.65, 117.46, 115.99, 115.45, 107.20, 77.50, 77.25, 76.99, 71.96, 69.19, 69.01, 45.44, 31.99, 29.74, 25.95, 22.99, 14.39. FT-IR (cm⁻¹) 3084, 2931, 2861, 2605, 2363, 2232, 1599, 1564, 1490, 1464, 1428, 1376, 1322, 1253, 1205, 1170, 1105, 1023, 924, 881, 835, 727, 522. ESI-MS: isotopic cluster peaking at m/z 537.48 [M+Na]⁺, 1051.92 [2M+Na]⁺. Anal. Calcd for C₃₁H₅₀N₂O₄: C, 72.33; H, 9.79; N, 5.44%. Found C, 72.38; H, 9.75; N, 5.40%.

Phthalocyanine (1). To phthalonitrile **7** (51 mg, 0.1 mmol) stirred in pentanol at 60 °C were added granules of lithium. The formation of lithium pentanolate was observable with an emission of hydrogen gas, followed immediately by the dark blue-green coloration of the reaction mixture. The reaction mixture was then slowly heated up to 130 °C and stirred overnight at this temperature. After cooling down and addition of ethanol and water, the waxy dark-blue phthalocyanine was filtered on paper and recovered in dichloromethane (100 mL). Water (100 mL) was added and the 2 phases were strongly stirred at room temperature overnight to remove the lithium; then dichloromethane was evaporated. The phthalocyanine was filtered and purified by silica gel column chromatography eluted by dichloromethane, yielding 30 mg of **1** (58%). C₁₂₄H₂₀₂N₈O₁₆, MW 2060.97. MS-MALDI-TOF (DHB) m/z 2061.51 [M+H]⁺. ¹H-NMR (500 MHz, CDCl₃, δ, ppm): 9.32, 8.89, 7.72 (12H, aromatics), 4.54 (s, 8H, C_{Ar}OC_H₂C), 3.71 (bs, 24H, CC_H₂OC₆H₁₃), 3.50 (t, 24H, -OC_H₂C₅H₁₁), 1.23-1.59 (m, 96, (CH₂)₄CH₃), 0.79 (s, 36H, CH₃), -0.5 (bs, 2H, NH). FT-IR (cm⁻¹) 2927, 2856, 1611, 1483, 1457, 1428, 1376, 1343, 1322, 1237, 1169, 1095, 1051, 1005, 922, 851, 823, 749, 721, 700, 648.

Twinned phthalocyanine (2). A mixture of bisdiiminoisoindoline **8**¹⁷ (45 mg, 0.25 mmol) and phthalonitrile **7** (15 equiv., 1.9 g, 3.7 mmol) was dissolved in dichloromethane, concentrated 3 times to ensure a homogeneous mixture, and then dried under vacuum. Pentanol (20 mL) and lithium were added. The emission of hydrogen gas was immediately followed by the dark blue-green coloration of the reaction mixture. The stirring continued overnight at 130 °C and the reaction mixture was cooled down and diluted with ethanol and water until complete precipitation of the phthalocyanines. After filtration, the phthalocyanines were recovered in dichloromethane (200 mL). Water (200 mL) was added and the 2 phases were strongly stirred at room temperature overnight; then dichloromethane was evaporated. The phthalocyanine mixture was filtered and cleaned by silica gel column chromatography eluted by dichloromethane. The clean mixture of phthalocyanines **1** and **2** was then separated by repeated loadings on an exclusion-diffusion chromatography, leading to **1** (512 mg) and **2** (65 mg, 8%). C₁₉₆H₃₀₆N₁₆O₂₄, MW 3270.62. MS-MALDI-TOF (DHB) m/z [M+H]⁺ 3271,83. FT-IR (cm⁻¹) 2927, 2856, 1611, 1483, 1458, 1375, 1344, 1313, 1282, 1234, 1169, 1097, 1019, 922, 823, 745, 727, 646.

Double-decker Eu(III) bisphthalocyanine (3). A mixture of dry europium acetate powder (8 mg, 0.025 mmol), DBU (0.2 mL), and phthalocyanine **1** (106 mg, 0.051 mmol) in 1-chloronaphthalene (1 mL) was refluxed for 5 h under nitrogen to give dark-green solution; then the solvent was removed under reduced pressure. The crude product was dissolved in dichloromethane, filtered and loaded on a silica gel column eluted by a mixture of CH₂Cl₂/MeOH (100:1). Further purification on preparative silica gel TLC (eluent CH₂Cl₂/*n*-hexane 100/1) led to a waxy dark green solid. Yield: 70 mg (32%). C₂₄₈H₄₀₀EuN₁₆O₃₂, MW 4269.88. MS-MALDI-TOF (DHB) m/z 4270.85 [M+H]⁺. FT-IR (cm⁻¹) 3045, 2954-2857, 1604, 1486, 1457, 1319, 1275, 1230, 1101, 1065, 925, 826, 756.

Conclusion

The interest in trialkylated pentaerythritol as a phthalocyanine substitution pattern lowering their aggregation has been evidenced by the preparation of the 3 phthalocyanines derivatives described in this paper: a symmetrically substituted monomeric, a twinned, and a double-decker derivative. We are now preparing metalated derivatives to investigate their relevant properties.

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