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Syntheses of novel non-aggregated binuclear phthalocyaninato vanadyl complexes using a palladium-catalyzed cross-coupling reaction

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Abstract

Novel soluble binuclear vanadylphthalocyanines linked by terminal diacetylene bridges, such as 1,4-bis{2′-[23″-(1″,2″,3″,4″,8″,9″,10″,11″,15″,16″,17″,18″-dodecakis-(2,2,2-trifluoroethoxy)phthalocyaninyl)]ethynyl}benzene divanadyl complex, 4,4′-bis{2″-[23-(1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninyl)]ethynyl}- benzophenone divanadyl complex and 3,6-bis{2′-[23″-(1″,2″,3″,4″,8″,9″,10″,11″,15″,16″,17″,18″-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninyl)]ethynyl}-9-tetradecylcarbazole divanadyl complex, were synthesized using a palladium-catalyzed, cross-coupling reaction between the corresponding terminal diacetylenes and an excess of 23-iodo-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninato vanadyl complex. A mononuclear vanadylphthalocyanine with a conjugated carbazole moiety namely, vanadyl 23-(2′-(6″-nitro-9″-tetradecyl-3″-carbazolyl)ethynyl)-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate, was also prepared for comparison. All target phthalocyanines were separated by common column chromatography and characterized by elemental analysis, IR and ^{1}H-NMR, UV–visible and fast-atom-bombardment mass spectroscopies. Their UV–visible absorption spectra in solution showed that the target phthalocyanine dimers were non-aggregated compounds.

Keywords: Binuclear vanadylphthalocyanine; Terminal diacetylene linkage; Synthesis; Palladium-catalyzed cross-coupling; Non-aggregated; Tetracosakis(2,2,2-trifluoroethoxy)-substituted

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1. Introduction

Since the discovery of the first phthalocyanine molecule in 1907, this class of organic compounds has continued to attract research attention in

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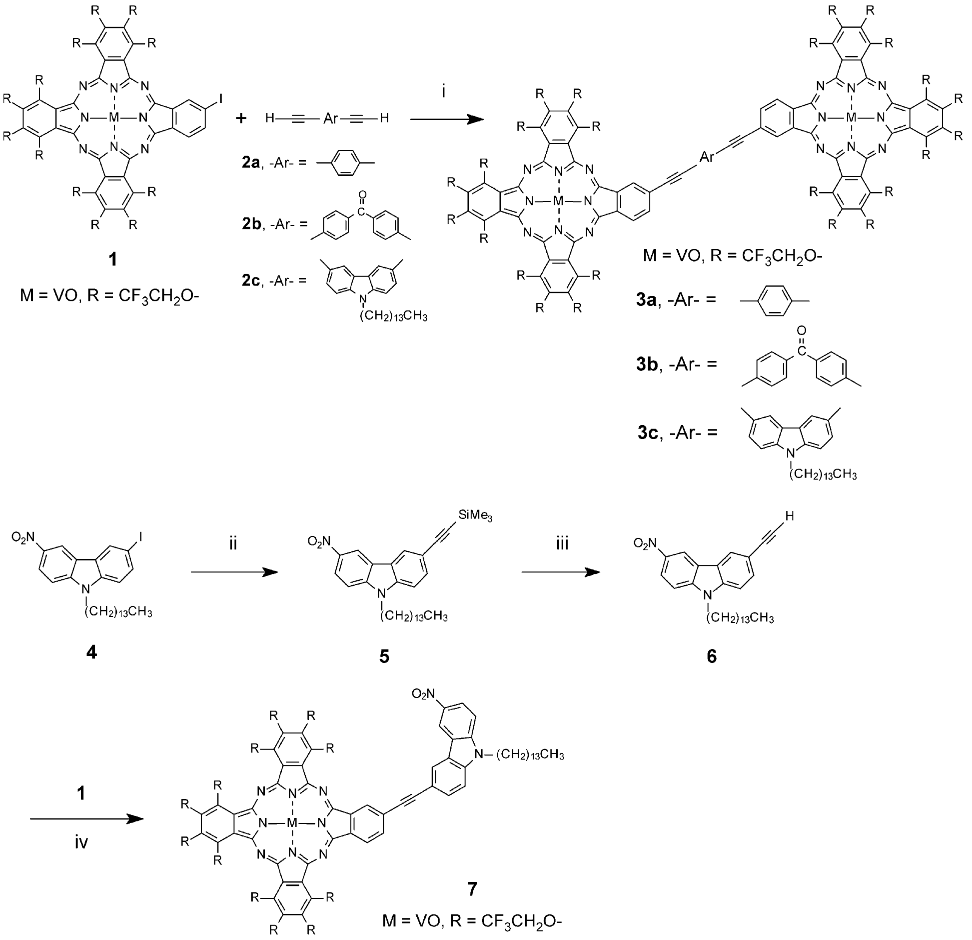
various fields such as dyes and pigments, semiconductors, catalysts, chemical sensors, liquid crystals and nonlinear optics [1–4]. To date, a great variety of symmetrical or pseudosymmetrical mononuclear phthalocyanines have been comprehensively studied [1–4]. Moreover, many phthalocyanine dimers and oligomers with various kinds of linkages have been reported [2–4]. Nevertheless, there have been a limited number of reports on the conjugated binuclear phthalocyanines [5–18], mainly because of their preparative difficulties. Such phthalocyanine dimers have rigid configurations and additional π-electron delocalization and often show spectroscopic, electrochemical and physical properties that differ significantly from the parent monomers. In particular, the conjugated phthalocyanine dimers with ethynyl linkages are potential electronic and photonic materials of interest, because such spacers are able to mediate unusually high excitonic and electronic coupling between the two phthalocyanine units [7,15–18]. They are also of great importance to a better understanding of the nature of phthalocyanines.

Binuclear phthalocyanines are usually prepared by one-step statistical synthesis employing a bis(1,3-diiminoisoindoline) and a differently substituted 1,3-diiminoisoindoline [5–11,14], or stepwise statistical condensation of two differently substituted 1,3-diiminoisoindolines [12,13]. Recently, monofunctional phthalocyanines with one iodo [16,17,19,20] or ethynyl [15,16,18,20] group, which were first used as building blocks for the syntheses of new mononuclear unsymmetrical phthalocyanines with extended π-conjugation, have also been employed in the synthesis of conjugated binuclear phthalocyanines through a catalyzed coupling reaction. The latter method proved much more efficient than the conventional one.

To search for new materials for nonlinear optics, we have been studying the preparation and nonlinear optical properties of unsymmetrically substituted phthalocyanines carrying donors and acceptor groups [21–28], and conjugated binuclear phthalocyanines as well [14]. Previously we have reported the synthesis of a series of new unsymmetrically dodecakis(2,2,2-trifluoroethoxy)-substituted metallophthalocyanines with extended exocyclic π-conjugation by the palladium(0)-catalyzed cross-coupling reaction between monoiodinated phthalocyanines and terminal acetylenes [25–27]. As an extension of our previous research, this paper reports the synthesis of some new, tetracosakis(2,2,2-trifluoroethoxy)-substituted vanadylphthalocyanine dimers linked by aryl terminal diacetylene bridges using the similar palladium(0)-catalyzed cross-coupling reaction (see Scheme 1). For comparison, a new dodecakis(2,2,2-trifluoroethoxy)-substituted vanadylphthalocyanine with a conjugated carbazole moiety was also prepared. There are several reasons why we designed and synthesized such phthalocyanine derivatives. First, we introduced twelve 2,2,2-trifluoroethoxy groups on three of the benzene subunits of each phthalocyanine moiety in order to enhance the solubility and suppress the intermolecular aggregation. Secondly, the introduction of different aryl terminal diacetylene linkages would provide new conjugated binuclear phthalocyanines with various configurations, which are very important in understanding the interactions between the two phthalocyanine cores. Moreover, we focused on the preparation of vanadylphthalocyanine dimers, because previously we found out the vanadyl phthalocyanine films have large third harmonic susceptibilities $\chi^{(3)}(-3\omega; \omega,\omega,\omega)$ among different metallophthalocyanine films [29,30]. Thus, the target vanadylphthalocyanine dimers are expected to be good candidates for third-order nonlinear optics. On the other hand, vanadylphthalocyanines show photoconductive properties [3,4,31], and 3-nitro-9-tetradecylcarbazole is a second-order nonlinear optical chromophore [32]; thus, the combination of such two moieties through ethynyl group would produce a new structure that should exhibit both photoconductive and second-order nonlinear optical properties. Such a multifunctional structure might be photorefractive [32]. This is why we synthesized compound **7**. In the present paper, the preparation, characterization and spectral properties of these novel binuclear and mononuclear vanadylphthalocyanine derivatives are described.

2. Results and discussion

The synthetic procedure of the target binuclear vanadylphthalocyanines **3a–c** is shown in Scheme 1.



Scheme 1. Reagents and conditions: (i) $(Ph_3P)_2PdCl_2$, CuI, Et_3N/THF, 40–50 °C, 27–48 h; 70–80 °C, 5–8 h; (ii) trimethylsilylacetylene, $(Ph_3P)_2PdCl_2$, CuI, Et_3N/THF, 40 °C, 4 h; (iii) NaOH/H_2O, THF/MeOH, r.t., 5 h; (iv) $(Ph_3P)_2PdCl_2$, CuI, Et_3N/THF, 30–40 °C, 40 h.

The preparation of 23-iodo-1,2,3,4,8,9,10,11,15,16,-17,18 - dodecakis(2,2,2 - trifluoroethoxy)phthalocyaninato vanadyl complex (**1**) was published in our previous study [25–27]. The intermediates 1,4-diethynylbenzene (**2a**) [33] and 4,4′-diethynylbenzophenone (**2b**) [34] were prepared according to the reference methods, and the synthesis of 3,6-diethynyl-9-tetradecylcarbazole (**2c**) [32,35] was reported in our previous work. The cross-coupling reaction between an excess of compound **1** and aryl terminal diacetylenes **2a–c** in triethylamine–tetrahydrofuran (2:3∼1:1, volume ratio) with bis(triphenylphosphine)palladium dichloride and copper(I) iodide as catalysts at 40–80 °C under a dry nitrogen atmosphere produced new binuclear phthalocyanines **3a–c** in 40–70% yield.

From Scheme 1, it is clear that the synthetic route through a palladium(0)-catalyzed coupling has several advantages over the conventional method to prepare binuclear phthalocyanines with terminal diacetylene linkages. Usually, a binuclear phthalocyanine was prepared by the mixed condensation between a bis(1,3-diiminoisoindoline) and a large excess of a 1,3-diiminoisoindoline in 2-(*N,N*-dimethylamino)ethanol under reflux [5–11,14]. This made the product mixture very complicated and the separation and purification of binuclear phthalocyanine quite difficult. However, in the palladium(0)-catalyzed coupling approach, mononuclear phthalocyanine was used as a building block, and binuclear phthalocyanines with unsaturated linkages were prepared under facile catalytic reaction conditions; therefore, the fast purification and isolation of the desired binuclear products was possible. Besides, the unreacted compound **1** could be recovered easily. As can be seen from the diversity of aryl terminal diacetylenes which undergo this reaction, the method is a powerful tool for preparing new binuclear phthalocyanines with different terminal diacetylene bridges to afford new advanced materials with unique electro-optical, magnetical or nonlinear optical properties.

Compound **7**, which is composed of a vanadylphthalocyanine unit and a 3-nitro-9-tetradecylcarbazole moiety, was prepared through the route depicted in Scheme 1. The synthesis of 3-iodo-6-nitro-9-tetradecylcarbazole (**4**) was described in our previous work [32]. The palladium(0)-catalyzed cross-coupling reaction between **4** and trimethylsilylacetylene in triethylamine–tetrahydrofuran (1:1, volume ratio) at 40°C for 4 h yielded 3-[2′-(trimethylsilyl)ethynyl]-6-nitro-9-tetradecylcarbazole (**5**) in 90.0% yield. 3-Ethynyl-6-nitro-9-tetradecylcarbazole (**6**) was obtained in 94.8% yield after the removal of trimethylsilyl group from **5** by treatment with dilute aqueous sodium hydroxide in tetrahydrofuran and methanol at room temperature for 5 h. The palladium(0)-catalyzed cross-coupling reaction between compounds **1** and **6** in triethylamine–tetrahydrofuran (1:1, volume ratio) at 30–40 °C gave the desired compound **7** in 75.0% yield after purification.

All final products were obtained as pure samples after purification via column chromatography on silica gel and then by recrystallization. Binuclear vanadylphthalocyanines **3a–c** and mononuclear product **7** were prepared as structural isomer mixtures. They were characterized by ^{1}H-NMR, IR and fast-atom-bombardment (FAB) MS spectroscopic methods, as well as by elemental analysis. All the analytical and spectral data are consistent with the predicted structures. It should be noted that the ^{1}H-NMR spectra of compounds **3a–c** and **7** are extremely broad because of the presence of the paramagnetic vanadium atom and the constitutional isomers [36]. Owing to the broad ^{1}H-NMR spectra, the aromatic protons of these binuclear and mononuclear vanadylphthalocyanines cannot be expected to be clearly resolved. Moreover, in the ^{1}H-NMR spectra of compounds **3a–c**, a marked difference in δ values corresponding to 32 and 16 OCH_2 protons was observed. This phenomenon may be attributed to the anisotropy effect of the induced magnetic field stemming from the cyclic current of 18 π-electrons of the phthalocyanine ring. Under the influence of such an induced magnetic field, an exocyclic proton is deshielded and has a relatively larger δ value, whereas an endocyclic proton is shielded and has a relatively smaller δ value. The magnitude of such a magnetic deshielding effect depends on the position of the exocyclic proton. For compounds **3a–c**, as a result of the strong steric hindrance effect between the neighboring 2,2,2-trifluoroethoxy groups at the 4- and 8-, 11- and 15-positions of the two phthalocyanine rings, the corresponding 16 OCH_2 protons are much closer to the phthalocyanine ring currents as compared to the other 32 OCH_2 protons. Thus, the 16 OCH_2 protons closer to the phthalocyanine ring would be affected by a far stronger magnetic deshielding effect, and the difference of such an effect between these OCH_2 protons, which arises from the unsymmetrical substitution of twelve 2,2,2-trifluoroethoxy groups on the phthalocyanine ring, would be much larger than that between the 32 OCH_2 protons farther from the phthalocyanine ring. In consequence, the corresponding δ values for the 16 OCH_2 protons at the 4,8,11,15-positions of the two phthalocyanine rings are significantly larger and more divergent than those for the 32 OCH_2 protons at the 1,2,3,9,10,16,17,18-positions. On the other hand, attempts to record the well-resolved ^{13}C-NMR spectra of these binuclear and mononuclear vanadylphthalocyanines were not successful.

Compounds **3a–c** and **7** show good solubility in common polar organic solvents such as diethyl ether, tetrahydrofuran, ethyl acetate and acetone. Figs. 1–3 show the UV–visible absorption spectra of compounds **3a–c** in comparison with vanadyl

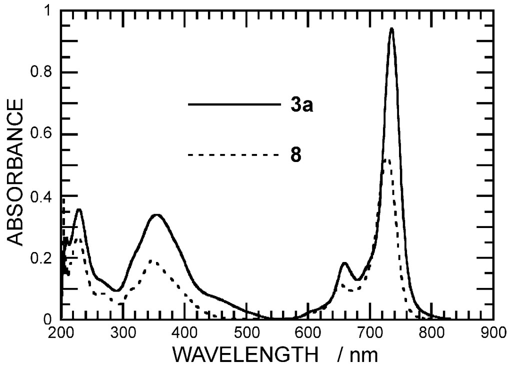


Fig. 1. Ultraviolet–visible absorption spectra of 1,4-bis{2′-[23″-(1″,2″,3″,4″,8″,9″,10″,11″,15″,16″,17″,18″-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninyl)]ethynyl}benzene divanadyl complex **3a** (2.32×10^{-6} M), and vanadyl 1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate **8** (3.18×10^{-6} M) in 1,4-dioxane.

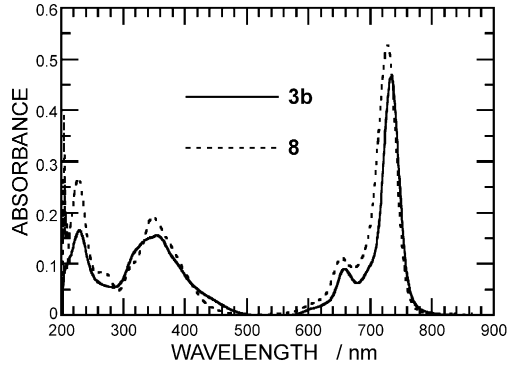


Fig. 2. Ultraviolet–visible absorption spectra of 4,4′-bis{2″-[23-(1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)-phthalocyaninyl)]ethynyl}benzophenone divanadyl complex **3b** (1.14×10^{-6} M), and vanadyl 1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate **8** (3.18×10^{-6} M) in 1,4-dioxane.

1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate (**8**) [24] in 1,4-dioxane, respectively. All three new binuclear phthalocyanines show sharp, characteristic absorptions in the Q-band region of around 736 nm without splitting, and in the B-band region of around 355 nm. Compared with the corresponding mononuclear phthalocyanine **8**, all three new binuclear phthalocyanines show a similar-shaped Q-band but with a slight redshift. Since the known phthalocyanine dimers usually show a Q-band absorption much broader than that of the corresponding mononuclear phthalocyanines [5–18], the spectral properties of compounds **3a–c** indicate that they are non-aggregated dimers in solution. The redshifts of Q-band for compounds **3a**, **3b** and **3c** in comparison with compound **8** are 6.5, 5.0 and 9.5 nm, respectively. These spectral results can be explained from the molecular structure of the phthalocyanine dimers. The strong steric hindrance effect of 12 bulky 2,2,2-trifluoroethoxy groups on three of the benzene units of the phthalocyanine ring enhances the solubility of these new phthalocyanine dimers and suppresses the intermolecular aggregation effect. The terminal diacetylene linkage between the two phthalocyanine units also prevents the intramolecular interaction between the two phthalocyanine units. This is why these phthalocyanine dimers show a Q-band absorption similar to that of the corresponding monomer **8**. On the other hand, the terminal diacetylene linkage between the two phthalocyanine units extends the exocyclic π-electron conjugation of the phthalocyanine unit, so these phthalocyanine dimers show a redshifted Q-band absorption with a shape similar to that of the monomer **8**. However, due to the rotation of ben-

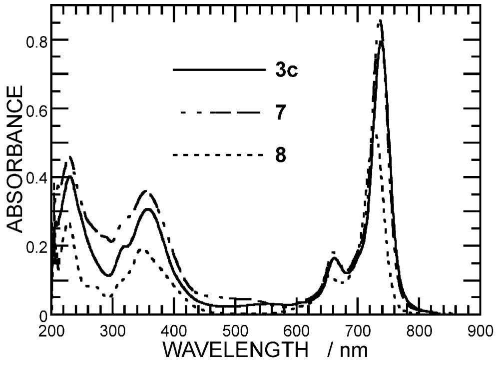


Fig. 3. Ultraviolet–visible absorption spectra of 3,6-bis{2′-[23″-(1″,2″,3″,4″,8″,9″,10″,11″,15″,16″,17″,18″-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninyl)]ethynyl}-9-tetradecylcarbazole divanadyl complex **3c** (2.05×10^{-6} M), vanadyl 23-(2′-(6″-nitro-9″-tetradecyl-3″-carbazolyl)ethynyl)-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate **7** (3.91×10^{-6} M) and vanadyl 1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate **8** (3.18×10^{-6} M) in 1,4-dioxane.

zene ring around the carbon–carbon triple bond, the effective conjugation between the phthalocyanine ring and exocyclic phenyl ring is reduced. Thus the redshifts of Q-band absorption for these phthalocyanine dimers over compound **8** should be small. This inference is in agreement with the spectral results of these phthalocyanine dimers. It should also be noted that quite different from dimers **3a** and **3b**, dimer **3c** shows a weak absorption in the window region between 450 and 600 nm. This phenomenon may be attributed to the existence of the carbazole moiety.

Fig. 3 also shows the UV–visible absorption spectrum of compound **7** in 1,4-dioxane. This novel unsymmetrical vanadylphthalocyanine with a carbazole moiety also exhibits typical absorptions in the Q-band region of around 736 nm without splitting and in the B-band region of around 355 nm. However, there is an absorption in the window region between 450 and 600 nm, due to the existence of the carbazole moiety. Compared with compound **8**, compound **7** shows a similar-shaped Q-band but with a redshift of 7.0 nm, as expected. Moreover, the UV–visible absorption spectrum of compound **7** is quite similar to that of the corresponding dimer **3c**. This phenomenon also demonstrates that compounds **3a–c** are non-aggregated dimers in solution.

In summary, three novel tetracosakis(2,2,2-trifluoroethoxy)-substituted binuclear vanadylphthalocyanines having aryl terminal diacetylene linkages, **3a–c**, were synthesized by a palladium(0)-catalyzed cross-coupling reaction between the corresponding terminal diacetylenes and 23-iodo-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninato vanadyl complex. Similarly, a novel mononuclear dodecakis(2,2,2-trifluoroethoxy)-substituted vanadylphthalocyanine with an exocyclic conjugated carbazole moiety, **7**, was also synthesized for comparison. All the target binuclear and mononuclear vanadylphthalocyanines were separated by common column chromatography and fully characterized. Their UV–visible absorption spectra in solution showed that dimers **3a–c** were non-aggregated phthalocyanine derivatives. The study on their nonlinear optical and other physical and chemical properties is now under way.

3. Experimental

IR spectra were recorded on a Shimadzu FTIR-4100 Fourier transform infrared spectrophotometer, using potassium bromide pellets. ^{1}H-NMR and ^{13}C-NMR spectra with tetramethylsilane as internal standard were recorded on a Jeol JNM-EX270 Fourier transform nuclear magnetic resonance spectrometer (270 MHz). Fast-atom-bombardment mass spectra (FAB-MS) with *m*-nitrobenzyl alcohol as a matrix were recorded on a Jeol JMS-HX110 mass spectrometer. Elemental analyses were carried out by the Microanalysis Laboratory of RIKEN (The Institute of Physical and Chemical Research). UV–visible absorption spectra were measured by a Shimadzu UV-3100 spectrophotometer in a quartz cell of path length 10 mm. Column chromatography was performed using silica gel of particle size 63–200 μm which was produced by Merck.

Anhydrous tetrahydrofuran was purchased from Kanto Chemical Co. Triethylamine was refluxed with sodium chips and distilled in an atmosphere of dry nitrogen gas before use. The solvents for UV–visible absorption measurement were of spectral grade and used without further purification. Other chemicals were of reagent grade and used as supplied.

23 - Iodo - 1,2,3,4,8,9,10,11,15,16,17,18 - dodecakis(2,2,2-trifluoroethoxy)phthalocyaninato vanadyl complex (**1**) [25-27] and 3,6-diethynyl-9-tetradecylcarbazole (**2c**) [32,35] were prepared according to the procedures published previously. 1,4-Diethynylbenzene (**2a**) [33] and 4,4′-diethynylbenzophenone (**2b**) [34] were prepared according to the reference methods. Bis(triphenylphosphine)palladium dichloride was prepared according to the literature [37,38].

3.1. *1,4-Bis{2′-[23″-(1″,2″,3″,4″,8″,9″,10″,11″,15″,16″,17″,18″-dodecakis(2,2,2-trifluoroethoxy)-phthalocyaninyl)]ethynyl}benzene divanadyl complex (**3a**)*

A typical procedure: in a 100-ml round-bottomed three-neck flask equipped with a nitrogen gas inlet, a reflux condenser and a magnetic stirring bar, was placed a mixture of vanadyl 23-iodo-

1,2,3,4,8,9,10,11,15,16,17,18 - dodecakis(2,2,2 - trifluoroethoxy)phthalocyaninate **1** (125 mg, 6.64×10^{-2} mmol), 1,4-diethynylbenzene **2a** (4.0 mg, 3.17×10^{-2} mmol), bis(triphenylphosphine)palladium dichloride (2.0 mg, 2.85×10^{-3} mmol) and copper(I) iodide (1.0 mg, 5.25×10^{-3} mmol). To this mixture, under dry nitrogen atmosphere, were added anhydrous tetrahydrofuran (30 ml) and anhydrous triethylamine (20 ml). The resulting reaction mixture was stirred at 45–50 °C under nitrogen gas for 48 h and then at 75–80 °C for 8 h. After the reaction mixture was cooled, the resulting brown precipitate was suction filtered and washed with tetrahydrofuran. The filtrate was condensed under reduced pressure, and the resulting residue was purified by column chromatography on silica gel with hexane/ethyl acetate (4:1, volume ratio) as the first eluent to give a green fraction of starting material **1** (53.0 mg), followed by eluting with hexane/ethyl acetate (3:1, volume ratio) to remove pale yellow impurities, and finally with 2:1 (volume ratio) hexane/ethyl acetate as an eluent to give a yellow-green fraction of the binuclear phthalocyanine. Recrystallization from ethyl acetate–hexane gave compound **3a** as a dark green microcrystalline solid, 49.0 mg (42.6%). IR: $\nu_{\max}/\mathrm{cm}^{-1}$ 3236 (=CH), 2968 (CH_2), 2928, 2862, 2210 (ethynyl), 1634, 1612 (C=C ring), 1488 (C=C ring), 1452, 1429 (CH_2), 1275, 1246 (C–O), 1160 (C–F), 1115 (ring), 1067, 1011 (V=O), 972 (C–O), 839 (CH_2), 760, 662. ^{1}H-NMR (CD_3COCD_3): δ 5.33 (m, 32H, OCH_2), 5.60–6.70 (br, 16H, OCH_2), 7.40–8.30 (br, 10H, H_{arom}). FAB-MS: m/z (%) 3633.4 (M^+, 100), 3550.4 (M^+–CF_3CH_2, 42.7). UV–visible (1,4-dioxane): $\lambda_{\max}$/nm (log[ε/dm^3 mol^{-1} cm^{-1}]) 735.5 (5.61), 659.0 (4.90), 354.0 (5.16), 229.5 (5.19). Anal. calcd for $C_{122}H_{58}N_{16}F_{72}O_{26}V_2$ (3633.66): C, 40.33; H, 1.61; N, 6.17; F, 37.64. Found: C, 40.98; H, 1.88; N, 5.89; F, 37.21.

*3.2. 4,4′-Bis{2″-[23-(1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy) phthalocyaninyl)]-ethynyl}benzophenone divanadyl complex (**3b**)*

Quantities: vanadyl 23-iodo-1,2,3,4,8,9,10,11, 15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate **1** (90 mg, 4.78×10^{-2} mmol), 4,4′-diethynylbenzophenone **2b** (5.0 mg, 2.17×10^{-2} mmol), bis(triphenylphosphine)palladium dichloride (2.0 mg, 2.85×10^{-3} mmol), copper(I) iodide (1.1 mg, 5.78×10^{-3} mmol), anhydrous tetrahydrofuran (20 ml) and anhydrous triethylamine (15 ml); reaction conditions: 40–45 °C, 44 h; 70–75 °C, 8 h. The experimental procedure was as described for the preparation of compound **3a**. The crude product was purified by column chromatography on silica gel with 4:1, 3:1 and 2:1 (volume ratio) hexane/ethyl acetate as the first, second and third eluents to give compound **1** (34.2 mg), pale yellow impurities, and a yellow-green fraction of the binuclear phthalocyanine, respectively. Recrystallization from ethyl acetate–hexane gave compound **3b** as a dark green microcrystalline solid, 54.0 mg (66.6%). IR: $\nu_{\max}/\mathrm{cm}^{-1}$ 3048 (=CH), 2977 (CH_2), 2357 (ethynyl), 1721, 1636, 1617, 1603 (C=C ring), 1487 (C=C ring), 1456, 1431 (CH_2), 1406, 1277, 1248 (C–O), 1163 (C–F), 1115 (ring), 1069, 1013 (V=O), 972 (C–O), 930, 853 (CH_2), 835, 762, 662. ^{1}H-NMR (CD_3COCD_3): δ 5.31 (m, 32H, OCH_2), 5.50–6.80 (br, 16H, OCH_2), 7.30–8.40 (br, 14H, H_{arom}). FAB-MS: m/z (%) 3737.9 (M^+, 100). UV–visible (1,4-dioxane): $\lambda_{\max}$/nm (log[ε/dm^3 mol^{-1} cm^{-1}]) 734.0 (5.61), 658.0 (4.90), 354.5 (5.13), 229.5 (5.16). Anal. calcd for $C_{129}H_{62}N_{16}F_{72}O_{27}V_2$ (3737.77): C, 41.45; H, 1.67; N, 6.00; F, 36.60. Found: C, 41.97; H, 1.75; N, 5.72; F, 36.08.

*3.3. 3,6-Bis{2′-[23″-(1″,2″,3″,4″,8″,9″,10″,11″,15″,16″,17″, 18″-dodecakis(2, 2, 2-trifluoroethoxy) phthalocyaninyl)]ethynyl}-9-tetradecylcarbazole divanadyl complex (**3c**)*

Quantities: vanadyl 23-iodo-1,2,3,4,8,9,10,11,15,16,17,18 - dodecakis(2,2,2 - trifluoroethoxy) phthalocyaninate **1** (150 mg, 7.97×10^{-2} mmol), 3,6-diethynyl-9-tetradecylcarbazole **2c** (15.0 mg, 3.65×10^{-2} mmol), bis(triphenylphosphine)palladium dichloride (2.0 mg, 2.85×10^{-3} mmol), copper(I) iodide (1.0 mg, 5.25×10^{-3} mmol), anhydrous tetrahydrofuran (35 ml), anhydrous triethylamine (30 ml); reaction conditions: 45–50 °C, 27 h; 75–80 °C, 5 h. The experimental procedure was as described for the preparation of compound **3a**. The crude product was purified by column chromatography on silica gel with 4:1, 3:1 and 1:1 (volume ratio) hexane/ethyl acetate as the first, second and third eluents to give compound **1** (51.0 mg), dark-green impurities, and a black-green fraction of the binuclear phthalocyanine, respectively. Recrystallization from ethyl acetate–hexane gave compound **3c** as a black green microcrystalline solid, 64.0 mg (44.8%). IR: ν_{max}/cm^{-1} 3224 (=CH), 2962, 2930, 2857 (CH_2), 2200 (ethynyl), 1717, 1608, 1595 (C=C ring), 1489 (C=C ring), 1456, 1429 (CH_2), 1275, 1246 (C–O), 1166 (C–F), 1110 (ring), 1067, 1011 (V=O), 971 (C–O), 853, 834 (CH_2), 807, 761, 662. ^{1}H-NMR (CD_3COCD_3): δ 0.92 (m, 3H, CH_3), 1.29 (m, 22H, $11\times CH_2$), 1.82 (m, 2H, CH_2), 4.20 (m, 2H, NCH_2), 5.28 (m, 32H, OCH_2), 5.60–6.80 (br, 16H, OCH_2), 7.20–8.80 (br, 12H, H_{arom}). FAB-MS: *m*/*z* (%) 3918.9 (M^+, 100), 3836.0 (M^+–CF_3CH_2, 31.0). UV–visible (1,4-dioxane): λ_{max}/nm (log[ε/$dm^3\ mol^{-1}\ cm^{-1}$]) 738.5 (5.59), 662.0 (4.90), 358.0 (5.18), 319.5 (4.99), 231.0 (5.29). Anal. calcd for $C_{142}H_{89}N_{17}F_{72}O_{26}V_2$ (3919.14): C, 43.52; H, 2.29; N, 6.08; F, 34.90. Found: C, 44.08; H, 2.47; N, 5.87; F, 34.88.

3.4. 3-[2′-(Trimethylsilyl)ethynyl]-6-nitro-9-tetradecylcarbazole (5)

Quantities: 3-iodo-6-nitro-9-tetradecylcarbazole **4** (4.00 g, 7.49 mmol), trimethylsilylacetylene (2.0 ml, ~14.4 mmol), bis(triphenylphosphine)palladium dichloride (300 mg, 0.427 mmol), copper(I) iodide (100 mg, 0.525 mmol), anhydrous tetrahydrofuran (100 ml), anhydrous triethylamine (100 ml); reaction conditions: 40 °C, 4 h. The experimental procedure was as described for the preparation of compound **3a**. The crude product was purified by column chromatography on silica gel with hexane/ethyl acetate/chloroform (8:1:1, volume ratio) as an eluent to yield a pale yellow solid. Recrystallization from ethyl acetate–hexane gave compound **5** as a pale-yellow microcrystalline solid, 3.40 g (90.0%). ^{1}H-NMR ($CDCl_3$): δ 0.30 (s, 9H, $Si(CH_3)_3$), 0.88 (t, $J=6.60$ Hz, 3H, CH_3), 1.24 (m, 22H, $11\times CH_2$), 1.88 (m, 2H, CH_2), 4.32 (t, $J=7.26$ Hz, 2H, NCH_2), 7.38 (d, $J_1=8.58$ Hz, 1H, 1-H_{arom}), 7.41 (d, $J_{1'}=9.24$ Hz, 1H, 8-H_{arom}), 7.66 (dd, $J_1=8.58$ Hz, $J_2=1.32$ Hz, 1H, 2-H_{arom}), 8.29 (d, $J_2=1.32$ Hz, 1H, 4-H_{arom}), 8.39 (*dd*, $J_{1'}=9.24$ Hz, $J_{2'}=2.31$ Hz, 1H, 7-H_{arom}), 8.98 (d, $J_{2'}=2.31$ Hz, 1H, 5-H_{arom}).

3.5. 3-Ethynyl-6-nitro-9-tetradecylcarbazole (6)

To a solution of 3-[2′-(trimethylsilyl)ethynyl]-6-nitro-9-tetradecylcarbazole **5** (3.20 g, 6.35 mmol) in tetrahydrofuran (50 ml) and methanol (20 ml), was added a solution of sodium hydroxide (1.0 g, 25 mmol) in water (2 ml). The resulting reaction mixture was stirred at room temperature for 5 h, and then poured into 500 ml of water. The resulting precipitate was collected by suction filtration and washed with water, then air-dried. The crude product was purified by column chromatography on silica gel with hexane/ethyl acetate (9:1, volume ratio) as an eluent to yield a pale yellow solid, 2.60 g (94.8%). ^{1}H-NMR ($CDCl_3$): δ 0.88 (t, $J=6.60$ Hz, 3H, CH_3), 1.24 (m, 22H, $11\times CH_2$), 1.88 (m, 2H, CH_2), 3.12 (*s*, 1H, ethynyl-H), 4.32 (t, $J=7.26$ Hz, 2H, NCH_2), 7.41 (d, $J_1=8.57$ Hz, 1H, 1-H_{arom}), 7.42 (d, $J_{1'}=8.91$ Hz, 1H, 8-H_{arom}), 7.68 (dd, $J_1=8.57$ Hz, $J_2=1.65$ Hz, 1H, 2-H_{arom}), 8.31 (d, $J_2=1.65$ Hz, 1H, 4-H_{arom}), 8.40 (dd, $J_{1'}=8.91$ Hz, $J_{2'}=2.31$ Hz, 1H, 7-H_{arom}), 8.99 (d, $J_{2'}=2.31$ Hz, 1H, 5-H_{arom}).

3.6. Vanadyl 23-(2′-(6″-nitro-9″-tetradecyl-3″-carbazolyl)-ethynyl)-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis-(2,2,2-trifluoroethoxy)phthalocyaninate (7)

Quantities: vanadyl 23-iodo-1,2,3,4,8,9,10,-11,15,16,17,18 - dodecakis(2,2,2 - trifluoroethoxy) - phthalocyaninate **1** (100 mg, 5.31×10^{-2} mmol), 3-ethynyl-6-nitro-9-tetradecycarbazole **6** (46 mg, 0.106 mmol), bis(triphenylphosphine)palladium dichloride (3.0 mg, 4.29×10^{-3} mmol), copper(I) iodide (2.0 mg, 1.05×10^{-2} mmol), anhydrous tetrahydrofuran (30 ml) and anhydrous triethylamine (30 ml); reaction conditions: 30–40 °C, 40 h. The experimental procedure was as described for the preparation of compound **3a**. The crude product was purified by column chromatography on silica gel with hexane/ethyl acetate (3:1, volume ratio) as an eluent to give a brown-green fraction of **7**. The crude unsymmetrical product was further purified by column chromatography on silica gel with 7:1 and 6:1 (volume ratio) hexane/ethyl acetate as the first and second eluents to remove the unreacted **1** and the impurities, followed by eluting with hexane/ethyl acetate (4:1, volume ratio) as the third eluent to give a brown-green solid. Recrystallization from ethyl acetate–hexane (1:18, three times) yielded a brown-green microcrystalline solid, 87 mg (75.0%). IR: ν_{max}/cm^{-1} 3248, 3019 (=CH), 2967, 2930, 2857 (CH_2), 2205 (ethynyl), 1629, 1608, 1599 (C=C ring), 1521 (NO_2), 1487 (C=C ring), 1453, 1428 (CH_2), 1328 (NO_2), 1275, 1246 (C–O), 1161 (C-F), 1113 (ring), 1066, 1011 (V=O), 972 (C–O), 854 (CH_2), 833, 760, 750, 663. ^{1}H-NMR (CD_3COCD_3): δ 0.83 (m, 3H, CH_3), 1.0–1.40 (m, 22H, 11×CH_2), 1.95 (m, CH_2), 4.60 (m, NCH_2), 5.34 (m, 16H, OCH_2), 5.60–6.60 (br m, 8H, OCH_2), 7.80–9.20 (br, 9H, H_{arom}). FAB-MS: m/z (%) 2186.3 (M^+, 100.0), 2103.3 (M^+–CF_3CH_2, 22.6), 2020.2 (M^+–2×CF_3CH_2, 5.7). UV–visible (1,4-dioxane): λ_{max}/nm (log[ε/dm^3 mol^{-1} cm^{-1}]) 736.0 (5.34), 660.5 (4.66), 354.5 (4.96), 229.0 (5.07), 210.5 (4.98). Anal. calcd for $C_{84}H_{62}N_{10}F_{36}O_{15}V$ (2186.36): C, 46.15; H, 2.86; N, 6.41; F, 31.28. Found: C, 46.26; H, 2.89; N, 6.25; F, 31.25.

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