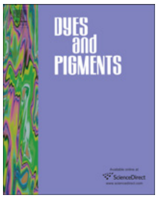
Dyes and Pigments 87 (2010) 10–16

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig



The synthesis and photophysical properties of zinc (II) phthalocyanine bearing poly(aryl benzyl ether) dendritic substituents

Yiru Peng [a,*], Hong Zhang [a], Haoling Wu [b], Baoquan Huang [a], Li Gan [a], Zhe Chen [c]

[a] *College of Chemistry & Materials Science, Fujian Normal University, Fujian Provincial Key Laboratory of Polymer Materials, Fuzhou 350007, China*
[b] *Affiliated First Hospital of Fujian Medical University, Fuzhou 350003, China*
[c] *College of Chemistry & Chemical Engineering, Xiamen University, Xiamen 361005, China*

ARTICLE INFO

Article history:
Received 26 October 2009
Received in revised form
19 January 2010
Accepted 20 January 2010
Available online 1 February 2010

Keywords:
Phthalocyanine
Dendrimer
Poly(aryl benzyl ester)
Cyano terminal groups
Synthesis
Photophysical property

ABSTRACT

Zinc (II) phthalocyanines carrying four poly(aryl benzyl ether) dendritic substituents with terminal cyano and carboxylic acid functionalities were synthesized and characterized using elemental analysis, ^{1}H NMR, IR, UV–vis and matrix-assisted laser-desorption ionization time-of-flight spectra. Phthalocyanines with terminal cyano groups were essentially non-aggregated in common organic solvents whilst the aqueous aggregation tendency of those which contained terminal carboxylic acid groups decreased with increasing size of the dendron. Photoinduced electron transfer in these compounds was investigated using a fluorescence quenching method, employing both neutral and cationic quenchers. Upon excitation of the dendritic subunits in DMSO, the cyano compounds underwent intermolecular energy transfer from the excited dendritic subunits to the phthalocyanine core which acted as an energy trap.

1. Introduction

Phthalocyanines and related macrocyclic compounds have found widespread application in various areas including liquid crystals, non-linear optical devices, catalysts, chemical sensors, data storage systems, electrochromic and photochromic materials and second generation photosensitizers for photodynamic therapy [1,2]. Numerous studies have been carried out to modify these macrocyclic compounds with the goal of moderating their properties and optimizing their performance for advanced materials.

In the context of photodynamic therapy, it is desired that phthalocyanines should not aggregate and have high solubility in aqueous media [3]. Molecular aggregation, which is an intrinsic characteristic of these large π-conjugated compounds, markedly shortens the phthalocyanine triplet state lifetime and reduces fluorescence quantum yield, thereby leading to a decrease in photodynamic therapy efficiency. Displaying high solubility in aqueous media would be beneficial not only for transportation of photosensitizers to malignant tissues by serum albumin but also for selective accumulation in the connective tissue which surround the tumor cells [4]. However, owing to hydrophobic interactions, stacking of phthalocyanines in aqueous media is particularly strong; consequently, hydrophilic and non-aggregated phthalocyanines are extremely rare despite their great potential application in photodynamic therapy.

Recently, phthalocyanines and their metal complexes encapsulated within the inner core of dendrimers that bear hydrophilic surface groups have been prepared and their high aqueous solubility, absence of aggregation and other interesting photophysical properties have been reported [5–15]. However, reports concerning this type of substituted phthalocyanine are relatively rare.

This paper concerns the synthesis and photophysical properties of two novel series of zinc (II) phthalocyanines containing four poly (aryl benzyl ether) dendritic substituents with terminal cyano and carboxylic acid functionalities. Both photoinduced intermolecular electronic transfer and energy transfer in these novel macromolecules are described.

2. Experimental

All reactions were carried out under nitrogen atmosphere in dried solvents. All chemicals were used as supplied by chemical companies. *n*-Pentanol and 1,8-diazabicyclo-(5,4,0)-undec-7-ene (DBU) were purchased from Aldrich. A Perkin–Elmer ATR Fourier transform infrared spectrometer was used for IR data collection.

---

[*] Corresponding author. Tel.: +86 591 8346 5225.
E-mail address: yirupeng@hotmail.com (Y. Peng).

0143-7208/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2010.01.016

^{1}H NMR spectra were recorded with a Bruker 400 MHz FT-NMR spectrometer. Matrix-assisted laser-desorption ionization time-of-flight (MALDI-TOF) spectra were obtained on a Bruker bench TOF mass spectrometer equipped with a standard UV-laser-desorption source, using dithranol as matrix. UV/Vis spectra were recorded on the Perkin–Elmer Lambda 9 UV/Vis/IR spectrometers. The Fluorescence spectra were recorded on the FL900/FS920 steady-state florescence spectrometers.

The scheme for synthesis of compounds (**3**)–(**11**) was listed in Fig. 1.

2.1. Synthesis of compound (*3*)

The mixture of 4-(bromomethyl) benzonitrile (**1**) (14.1 g, 72.0 mmol), 3,5-dihydroxybenzylalcohol (**2**) (4.9 g, 35.0 mmol), K_2CO_3 (12.1 g, 87.0 mmol), and 18-crown-6 (1.85 g, 7.0 mmol) in tetrahydrofuran (THF) (50 mL) was heated at reflux and stirred vigorously under nitrogen for 24 h. The mixture was allowed to cool and evaporated to dryness under reduced pressure. The residue was dissolved in water and $CHCl_3$ (100 mL) (1:1 (v/v)) and the aqueous layer extracted with $CHCl_3$ (30 mL) for three times. The combined organic layers were then dried over $MgSO_4$ and evaporated to dryness. The crude product was recrystallized from hexane/CH_2Cl_2 (50 mL) (2:3 (v/v)) to give (**3**) as white colourless crystals. Yield: 89%; mp: 144–146 °C; Analysis Calcd. for $C_{23}N_2H_{18}O_3$, C: 74.58, H: 4.89, N: 7.55. Found: C: 74.59, H: 4.86, N: 7.57. IR/cm^{-1}: 3400, 2900–2800, 2230, 1600, 1442, 1414, 1317, 1296, 1213, 1150, 1073, 1020, 822. ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.85–7.87 (m, 4H, CNPh–H), 7.61–7.63 (d, $J = 8$ Hz, 4H, CNPh–H), 6.54 (s, 2H, Ar–H), 6.60 (s, 1H, Ar–H), 5.20 (s, 4H, $CNPhCH_2$), 4.42 (s, 2H, CH_2OH). ESI-MS (*m*/*z*): 370. Found: 393 [M + Na]$^+$.

2.2. Synthesis of compound (*4*)

Carbon tetrabromide (5 g, 15.0 mmol) and triphenylphosphine (caution: stable; incompatible with oxidizing agents, acids; 3.7 g, 15.0 mmol) were added to a solution of (**3**) (15 g, 13.5 mmol) in the minimum amount of THF (10 mL), and the reaction mixture was stirred at room temperature under nitrogen. The reaction mixture changed from a transparent solution to a white solution with a precipitate forming over time. The aqueous layer was extracted with $CHCl_3$ (30 mL) for three times, and the $CHCl_3$ extracts were combined, dried and concentrated under reduced pressure. The crude product was recrystallized from hexane/CH_2Cl_2 (100 mL) (3:7 (w/w)) to give (**4**) as white powder. Yield: 83%; Analysis Calcd. for $C_{23}N_2H_{17}O_2Br$, C: 63.58, H: 3.79, N: 6.56. Found: C: 63.74, H: 3.93, N: 6.47. IR/cm^{-1}: 3400, 2900–2800, 2230, 1600, 1443, 1416, 1318, 1295, 1214, 1150, 1073, 1020, 822. ^{1}H NMR (DMSO-d$_6$, 400 MHz, δ/ppm): 7.66–7.68 (d, $J = 8$ Hz, 4H, CNPh–H), 7.50–7.52 (d, $J = 8$ Hz, 4H, CNPh–H), 6.61 (s, 2H, Ar–H), 6.47 (s, 1H, Ar–H), 5.00 (s, 4H, $CNPhCH_2$), 4.63 (s, 2H, CH_2OH). ESI-MS (*m*/*z*), 433. Found: 457 [M + Na]$^+$.

2.3. Synthesis of compound (*5*)

The mixture of (**4**) (5 g, 11.1 mmol), 3,5-dihydroxybenzylalcohol (**2**) (0.74 g, 5.0 mmol), K_2CO_3 (12.1 g, 87.0 mmol), and 18-crown-6 (0.29 g, 1.07 mmol) in acetone (50 mL) was heated at reflux and stirred vigorously under nitrogen for 48 h. The mixture was allowed to cool and evaporated to dryness under reduced pressure. The residue was dissolved in water and $CHCl_3$ (100 mL) (1:1 (v/v)) and the aqueous layer extracted with $CHCl_3$ (30 mL) for three times. The combined organic layers were then dried over $MgSO_4$ and evaporated to dryness. The crude product was recrystallized from hexane/CH_2Cl_2 (100 mL) (2:3 (v/v)) to give (**5**) as a colourless glass. Yield: 75%. Analysis Calcd. for $C_{53}N_4H_{39}O_3$: C: 75.58, H: 4.51, N: 6.62. Found: C: 75.36, H: 4.74, N 6.64. IR/cm^{-1}: 3400, 2930, 2230, 1500, 1450, 1415, 1318, 1298, 1214, 1160, 1050, 822. ^{1}H NMR (DMSO-d$_6$, 400 MHz, δ/ppm): 7.84–7.85 (m, 8H, CNPh–H), 7.62 (s, 8H, CNPh–H), 6.73 (s, 4H, Ar′–H), 6.65 (s, 2H, Ar–H), 6.58 (s, 2H, Ar′–H), 6.49 (s, 2H, Ar–H), 5.21 (s, 8H, $CNPhCH_2$), 5.01 (s, 4H, CH_2OH), 4.44 (s, 2H, CH_2OH). ESI-MS (*m*/*z*), 844. Found: 867 [M + Na]$^+$.

2.4. Synthesis of compound (*6*)

Anhydrous potassium carbonate (0.62 g, 4.50 mmol) was added to a mixture of 4-nitrophthalonitrile (0.52 g, 3.02 mmol) and (**3**) (1.11 g, 3.00 mmol) in DMF (20 mL). The mixture was heated at 60 °C with stirring overnight, and then poured into an ice-water mixture (100 mL). The precipitate formed was filtered off and purified by recrystallization using methanol (50 mL) as solvent to give (**6**) as a white solid. Yield: 50%; mp: 222–224 °C. Analysis Calcd. for $C_{31}N_4H_{20}O_3$, C: 75.00, H: 4.23, N: 11.29. Found: C: 74.99, H: 4.25, N: 11.32. IR/cm^{-1}: 3400–3300, 3090, 2910–2800, 2228, 1599, 1443, 1416, 1318, 1295, 1214, 1165, 1060, 1020, 822. ^{1}H NMR (DMSO-d$_6$, 400 MHz, δ/ppm): 8.06–8.08 (d, $J = 8$ Hz, 1H, Ar–H), 7. 84–7.87 (t, 5H, CNPh–H), 7.61–7.63 (d, $J = 8$ Hz, 4H, CNPh–H), 7.49–7.51 (d, $J = 8$ Hz, 1H, Ar–H), 6.69 (s, 1H, Ar–H), 6.74 (s, 1H, Ar–H), 5.20–5.22 (d, $J = 8$ Hz, 4H, $PhCH_2O$), 5.10 (s, 2H, $PhCH_2O$).

ESI-MS (*m*/*z*), 496. Found: 519 [M + Na]$^+$.

2.5. Synthesis of compound (*7*)

According to the above procedure, 4-nitrophthalonitrile (340 mg, 2.02 mmol) was treated with (**5**) (2.0 g, 2.0 mmol) and anhydrous potassium carbonate (0.62 g, 4.5 mmol) in DMF (10 mL) to give (**7**) as a white solid. Yield: 60%. Analysis Calcd. for $C_{61}N_6H_{42}O_7$, C: 75.28, H: 4.23, N: 8.66. Found: C: 75.39, H: 4.33, N: 8.65. IR/cm^{-1}: 3300, 2932, 2230, 1599, 1450, 1430, 1318, 1295, 1250, 1160, 1060, 1020, 822. ^{1}HNMR (DMSO-d$_6$, 400 MHz, δ/ppm): 8.02–8.05 (d, $J = 12$ Hz, 1H, CNPh–H), 7. 83–7.85 (d, $J = 8$ Hz, 9H, $(CN)_2Ph$–H), 7.59–7.61 (d, $J = 8$ Hz, 8H, CNPh–H), 7.47–7.50 (d, $J = 12$ Hz, 1H, $(CN)_2Ph$–H), 6.71 (s, 4H, Ar–H), 6.69 (s, 3H, Ar–H), 6.65 (s, 1H, Ar–H), 5.20 (s, 0H, $CNPhCH_2O$), 5.02 (s, 4H, $PhCH_2O$). ESI-MS (*m*/*z*), 971. Found: 994 [M + Na]$^+$.

2.6. Synthesis of compound (*8*)

A mixture of (**6**) (0.2 g, 0.4 mmol) and Zn(OAc) • $2H_2O$ (0.02 g, 0.10 mmol) in *n*-pentanol (10 mL) was heated at 130 °C, and then a few drops of DBU were added. The mixture was heated at 150 °C with stirring overnight. The volatiles were then removed under reduced pressure to give a greenish blue solid, which was chromatographed twice with ethyl acetate/hexanes (9:1(v/v)) as eluent. The crude product obtained was dissolved in a minimum amount of THF to which MeOH (30 mL) and H_2O (70 mL) were added to induce precipitation. A greenish blue solid was obtained after filtration and drying in vacuo. Yield: 60%; Analysis Calcd. for $C_{124}N_{16}H_{80}O_{12}Zn$: C: 72.62, H: 3.90, N: 10.93. Found: C: 72.64, H: 3.89, N: 10.91. IR/cm^{-1}: 3300, 2920, 2230, 1600, 1450, 1430, 1318, 1295, 1250, 1165, 1060, 1020, 822, 580. ^{1}H NMR (DMSO-d$_6$, 400 MHz, δ/ppm): 7.67 (s, 4H, Pc–H), 7.63–7.65 (d, $J = 8$ Hz, 16H, Ar–H), 7.47–7.49 (d, $J = 8$ Hz, 16H, Ar–H), 7.24–7.25 (d, $J = 4$ Hz, 4H, Pc–H), 7.16–7.17 (d, $J = 4$ Hz, 4H, Pc–H), 6.57 (s, 8H, Ar–H), 6.50 (s, 4H, Ar–H), 5.05 (s, 24H, $PhCH_2O$). MS (MALDI-TOF) (*m*/*z*), 2049. Found: 2068 [M + H_3O]$^+$.

2.7. Synthesis of compound (*9*)

Using the above procedure, Zn(OAc) • $2H_2O$ (0.02 g, 0.10 mmol) was treated with (**7**) (0.39 g, 0.40 mmol) and DBU in *n*-pentanol

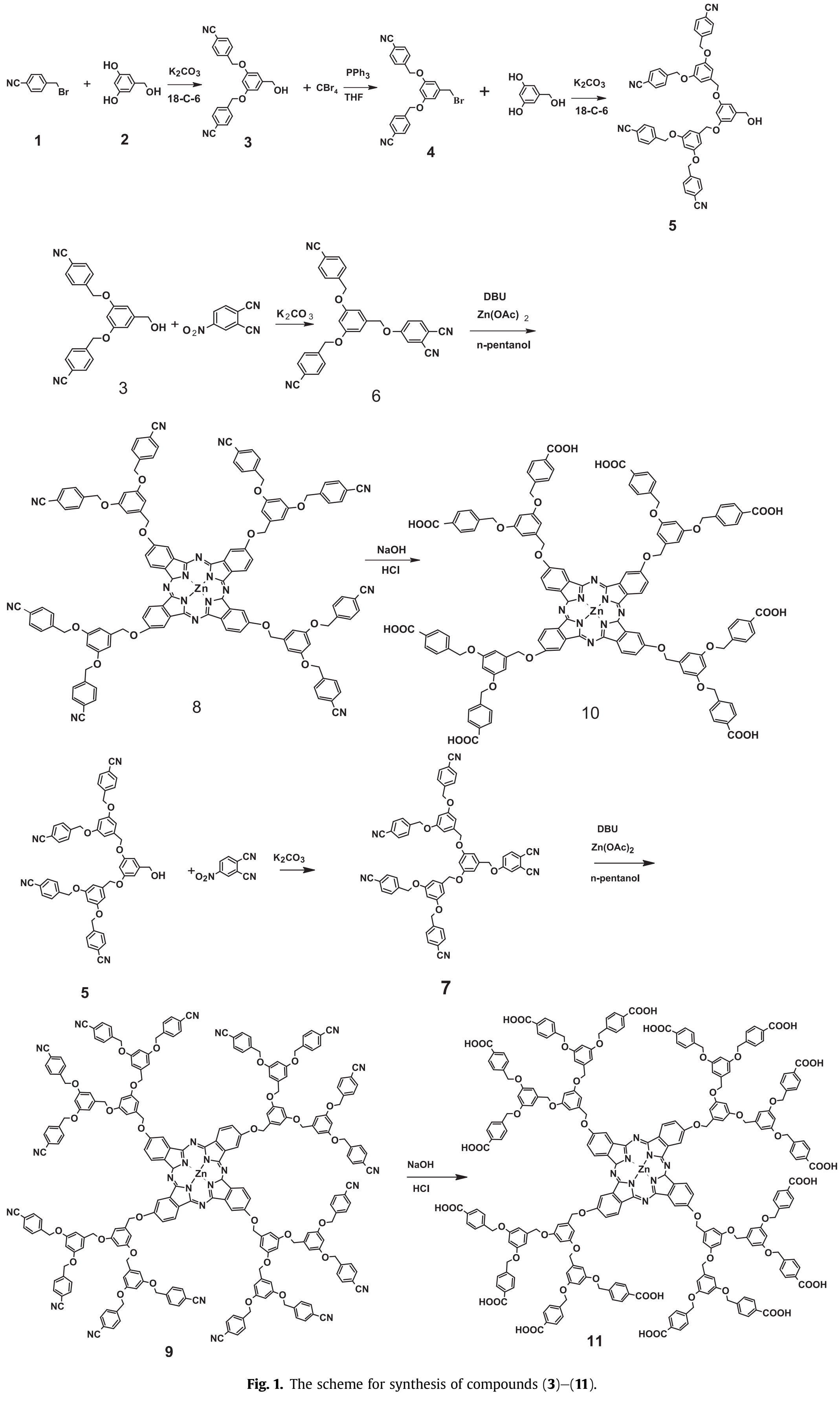


Fig. 1. The scheme for synthesis of compounds (**3**)–(**11**).

(15 mL) to give (**9**) as a dark green solid. The volatiles were then removed under reduced pressure to give a greenish blue solid, which was chromatographed twice with ethyl acetate/hexanes (9:1 (v/v)) as eluent. A greenish blue solid was obtained after filtration and drying in vacuo. Yield: 80%; Analysis Calcd. for $C_{244}N_{24}H_{168}O_{28}Zn$: C: 74.11, H: 4.18, N: 8.48. Found: C: 74.15, H: 4.25, N: 8.51. IR/cm^{-1}: 3300, 2920–2800, 2230, 1600, 1450, 1430, 1251, 1153, 1067, 822, 580. ^{1}H NMR (DMSO-d$_6$, 400 MHz, δ/ppm): 7.80–7.82 (d, $J = 8$ Hz, 32H, CNPh–H), 7.56–7.58 (d, $J = 8$ Hz, 32H, CNPh–H), 7.38 (s, 4H, Pc–H), 7.29 (s, 4H, Pc–H), 7.19–7.21 (d, $J = 8$ Hz, 4H, Pc–H), 6.69 (s, 16H, Ar–H), 6.61 (s, 12H, Ar–H), 6.57 (s, 8H, Ar–H), 5.17 (s, 40H, $PhCH_2O$), 4.99 (s, 16H, $PhCH_2O$). MS (MALDI-TOF) (*m*/*z*): 3949. Found: 3968 $[M + H_3O]^+$.

2.8. *General procedure for hydrolysis of compounds (**8**)–(**9**) to form compounds (**10**)–(**11**)*

A mixture of compound (**8**) (400 mg) in 1 mol L^{-1} NaOH (30 mL) was stirred at 100 °C for 7 h, and then the precipitate formed in 1 mol L^{-1} HCl (100 mL) was filtered off. The resulting blue solid contaminated with NaOH was dissolved in water (30 mL), and several drops of 1 mol L^{-1} HCl were added until the pH reached about 7. Ethanol (100 mL) was then added to precipitate the salt, and the mixture was allowed to stand overnight. The corresponding product (**10**) was collected by filtration and dried in vacuo. By using the similar procedure, compound (**9**) was hydrolyzed to obtain (**11**).

A mixture of compound (**9**) (780 mg) in 1 mol L^{-1} NaOH (30 mL) was stirred at 100 °C for 7 h, and then the precipitate formed in 1 mol L^{-1} HCl (100 mL) was filtered off. The resulting blue solid contaminated with NaOH was dissolved in water (30 mL), and several drops of 1 mol L^{-1} HCl were added until the pH reached about 7. Ethanol (100 mL) was then added to precipitate the salt, and the mixture was allowed to stand overnight. The corresponding product (**11**) was collected by filtration and dried in vacuo. The yield of (**10**) was 82%, and that of (**11**) was 80%. For (**10**), Analysis Calcd. for $C_{124}N_8H_{88}O_{28}Zn$: C: 70.02, H: 4.14, N: 5.27. Found: C: 70.01, H: 4.16, N: 5.29. IR/cm^{-1}: 3300, 2930, 1690, 1600, 1450, 1430, 1318, 1295, 1250, 1153, 1067, 1020, 822, 580; ^{1}H NMR (DMSO-d$_6$, 400 MHz, δ/ppm): 7.90–7.92 (d, $J = 8$ Hz, 16H, HOOCPh–H), 7.50–7.52 (d, $J = 8$ Hz, 16H, HOOCPh–H), 7.18 (s, 4H, Pc–H), 7.04–7.06 (d, $J = 8$ Hz, 4H, Pc–H), 6.92–6.93 (d, $J = 4$ Hz, 4H, Pc–H), 6.71 (s, 4H, Ar–H), 6.55 (s, 4H, Ar–H), 5.23 (s, 4H, $PhCH_2O$), 5.14 (s, 4H, $PhCH_2O$), 5.08 (s, 4H, $PhCH_2O$). MS (MALDI-TOF) (*m*/*z*), 2201. Found: 2203 $[M + 2]^+$. For (**11**), Analysis Calcd. for $C_{244}N_8H_{184}O_{44}Zn$: C: 68.66, H: 4.24, N: 2.58. Found: C: 68.84, H: 4.33, N: 2.63. IR/cm^{-1}: 3300, 3040, 2930, 1700, 1600, 1450, 1400, 1250, 1160, 1053, 1020, 822, 580. ^{1}H NMR (DMSO-d$_6$, 400 MHz, δ/ppm): 7.94–7.96 (d, $J = 8$ Hz, 32H, HOOCPh–H), 7.78–7.80 (s, 4H, Pc–H), 7.53–755 (d, $J = 8$ Hz, 32H, HOOCPh–H), 7.31 (s, 4H, Pc–H), 7.11–7.14 (d, $J = 12$ Hz, 4H, Pc–H), 6.73 (s, 16H, Ar–H), 6.72–6.71 (d, $J = 4$ Hz, 12H, Ar–H), 6.66 (s, 8 H, Ar–H), 5.18 (s, 32H, $PhCH_2O$), 5.12 (s, 8H, $PhCH_2O$), 5.12 (s, 8H, $PhCH_2O$). MS (MALDI-TOF) (*m*/*z*), 4253. Found: 4253 $[M]^+$.

3. Results and discussion

3.1. *Synthesis and characterization*

The preparation of dendritic zinc (II) phthalocyanines commenced with the synthesis of cyano-terminated dendritic phenols. The cyano-terminated dendritic phenols (**3**) and (**5**) were prepared by the convergent growth approach involving repetitive sequential growth and activation steps [16]. Briefly, 4-(bromomethyl)benzonitrile (**1**) was coupled to the monomer unit, 3,5-dihydroxybenzyl alcohol (**2**), in the presence of potassium carbonate, in acetone at reflux to give the first generation alcohol (**3**) in 89% yield. Reaction of (**3**) with carbon tetrabromide/triphenylphosphine regenerated the benzyl bromide site at the focal point to give (**4**). Coupling of (**4**) to the monomer unit (**2**), through reaction with potassium carbonate afforded the second generation dendritic alcohol (**5**). Cyano groups were chosen as the terminal functionalities because of their strong electron withdrawal ability and their stability to the reaction conditions used for dendritic growth with 3,5-dihydroxybenzyl alcohol as the monomer unit [17]. In the above reactions including all the coupling reactions to the monomer unit, no tri-O-alkylated or C-alkylated products were observed [18]. Treatment of these dendritic alcohols with 4-nitrophthalonitrile in the presence of K_2CO_3 led to nucleophilic aromatic substitution giving the corresponding dendritic phthalonitriles (**6**)–(**7**) in good yields. Cyclization of these phthalonitriles (**6**)–(**7**) with $Zn(OAc) \bullet 2H_2O$ in the presence of a strong organic base (DBU) in *n*-pentanol gave the corresponding dendritic zinc (II) phthalocyanines (**8**)–(**9**) with cyano terminal groups as mixtures of constitutional isomers. Upon treatment with NaOH in water, compounds (**8**)–(**9**) were hydrolyzed to afford corresponding water-soluble zinc (II) phthalocyanines (**10**)–(**11**) with carboxylic acid terminal groups in almost quantitative yields.

Compounds (**8**)–(**9**) were highly soluble in most organic solvents such as $CHCl_3$, CH_2Cl_2, acetone, DMF and DMSO. With a substantial number of hydrophilic moieties, compounds (**10**)–(**11**) possessed good solubility in aqueous media.

The structures of compounds (**3**)–(**11**) were characterized by a combination of methods including elemental analysis, ^{1}H NMR, IR, and UV–vis, ESI-MS and MALDI-TOF mass spectrometry.

Intense singly charged molecular ions peaks were observed for the MALDI-TOF spectra of all phthalocyanines (**8**)–(**11**) with dithranol as the matrix.

Dendritic phthalocyanines (**8**)–(**11**) gave similar IR spectra. After dendritic phthalonitriles (**6**)–(**7**) having been converted into corresponding zinc (II) phthalocyanines (**8**)–(**9**), the stretching vibration absorption of the phthalocyanines at 1600–1610 and 1520–1530 cm^{-1} appeared, indicating of the formation of phthalocyanines. Moreover, the vibrations at 2800–3000 and 1060–1165 cm^{-1} belonging to the characteristic stretching vibration of the submethyls and C–O–C of the substituted dendritic structure were also observed. Upon treatment with NaOH, the terminal cyano functional groups in (**8**)–(**9**) underwent hydrolysis yielding corresponding compounds (**10**)–(**11**). The intense stretching band at 2237 cm^{-1} assigned to the cyano groups of (**8**)–(**9**) disappeared, while two intense signals at 1600 and 1318 cm^{-1} emerged which could be assigned to the ν_{asy} and ν_{sym} stretching for the carboxylic acid groups in (**10**)–(**11**), indicating the hydrolysis was essentially complete.

Compounds (**8**)–(**11**) were found to be pure by ^{1}H NMR with both the dendritic substituents and phthalocyanine ring protons in their respective aromatic and alkyl regions. The ^{1}H NMR spectrum of the second generation dendritic zinc (II) phthalocyanine (**9**) presented a great deal of structural information. As a consequence

Table 1
Photophysical properties of dendritic phthalocyanines (**8**)–(**11**).

Compounds	Q-band/nm (log ε)	λ_{em}[a]	τ_s (ns)	Φ_f[b]
(**8**)	685 (6.72)	687–693	5.06	0.45
(**9**)	686 (6.27)	704	3.62	0.44
(**10**)	686 (5.99), 626[c]	678	5.37, 2.73[d]	0.86
(**11**)	684 (6.09), 626 (5.67)[c]	709	0.49, 0.39[d]	0.71

[a] Excited at 610 nm.
[b] Relative to ZnPc ($\Phi_f = 0.32$ in DMSO).
[c] Due to aggregated species in water.
[d] In water.

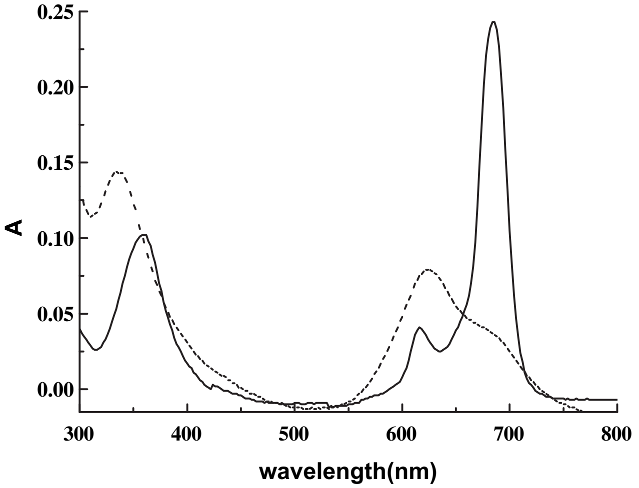


Fig. 2. UV/Vis spectra of (**10**) (2×10^{-5} mol L^{-1}) (– –) and (**11**) (2×10^{-5} mol L^{-1}) (—) in water.

of the strong electron-withdrawing effect of the cyano groups, the lowest shifted signals at 7.80–7.82 and 7.56–7.58 ppm were assigned to exterior aromatic protons of the dendritic substitutions with cyano terminal groups. Three sets of resonances were observed at 7.38, 7.29 and 7.19–7.21 ppm integrating for four protons each, making a total of 12 protons expected for the phthalocyanine ring protons. The resonances at 6.69, 6.61 and 6.57 ppm were assigned to the signals of the interior aromatic protons. The singlet at 5.17–4.99 ppm was due to the benzylic methylene protons. Integration of the signals in the aromatic region and comparison with other resonances in alkyl region allowed the structure of (**9**) to be determined. Confirmation the structures for the other phthalocyanines (**8**), (**10**) and (**11**) was similarly accomplished. The layers of the monomer units for the different generations were seen as additional peaks in the ^{1}H NMR spectra slightly shifted from one another.

The UV–vis spectrum of (**8**) in DMSO exhibited a strong Q-band at 685 nm in addition to the UV bands at 290 nm due to the dendritic substituents. When the concentrations of (**8**) increased from 2.0×10^{-7} to 2.2×10^{-5} mol dm^{-3}, (**8**) always exhibited a narrowed Q-band at 685 nm, suggesting that molecular aggregation was not significant for this compound in this concentration range. The absorption spectra of (**9**) were very similar to that of (**8**), and the data were summarized in Table 1.

The absorption spectra of (**10**)–(**11**) in water are shown in Fig. 2, and the photophysical data were also compiled in Table 1. The spectrum of (**10**) showed a broad signal with a maximum at 626 nm, which could be attributed to a dimeric species [19] indicating that (**10**) was highly aggregated in water even under dilute conditions. The UV–vis spectrum of (**11**) in aqueous solution exhibited a broad band at 626 nm. But after sonication or being heated to ca. 70 °C, the spectrum changed remarkably, leading to a monomer like spectrum at 684 nm. The spectrum with a maximum at 684 nm indicating that (**11**) was relatively free from molecular aggregation under these conditions. The absorption spectra of (**10**)–(**11**) in DMSO indicated that both compounds existed mainly as a monomeric species.

3.2. Photophysical properties

Upon excitation at 610 nm, compounds (**8**)–(**9**) showed fluorescence emission spectra at 687–693 and 704 nm in DMSO with quantum yields of 0.45 and 0.44 (with relative to ZnPc in DMSO $\Phi_f = 0.32$), respectively. The fluorescence emission spectra of water-soluble phthalocyanines (**10**)–(**11**) in water were at 678 and 709 nm with quantum yields of 0.86 and 0.71, respectively. The singlet excited lifetimes (τ_s) were determined by time-resolved experiments in which the fluorescence decay profiles were found to fit to a mono-exponential function $[f(t) = A + B_1 e^{-t/\tau 1} + B_2 e^{-t/\tau 2} + B_3 e^{-t/\tau 3} + B_4 e^{-t/\tau 4}]$. These values were listed in Table 1. Having a larger number of dendritic substituents, compounds (**9**) and (**11**) were relatively non-aggregated in solvents, showed much stronger emission, and located at slightly red shifted position. These results showed that the size of the dendrons had a significant influence on the phthalocyanines photophysical properties. Fluorescence of phthalocyanines was rarely seen in aqueous media [20]. To our knowledge, the intense fluorescence observed for phthalocyanines (**10**) and (**11**) in water without the aid of surfactants is virtually unprecedented.

Using anthraquinone as the quencher, the intensities of fluorescence and the rate of fluorescence quenching of compounds (**8**)–(**9**) were measured in DMSO. With increasing concentration of

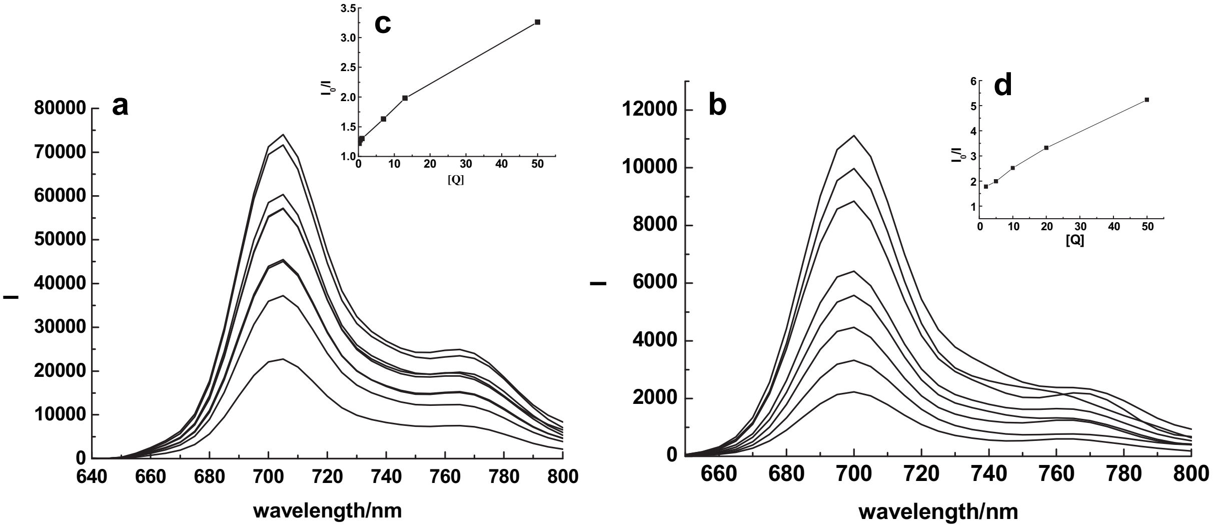


Fig. 3. Fluorescence spectra of (**8**) (a) and (**9**) (b) quenching by anthraquinone in DMSO. $c_{(8),(9)} = 2.0 \times 10^{-5}$ mol L^{-1} in all cases. $c_{anthraquinone} = (\times 10^{-5}$ mol $L^{-1})$ from up to down: 0, 0.2, 0.5, 1, 7, 13, 50. Inset plots: Stern–Volmer plots for the fluorescence quenching of (**8**) (c) and (**9**) (d) in DMSO.

Table 2
Rate constants for quenching of the fluorescence of (**8**)–(**9**) in DMSO and (**10**)–(**11**) in water.

Compounds	Quencher	$K_{SV} \times 10^3$ (L mol^{-1})	$K_q \times 10^{11}$ (L mol^{-1} s^{-1})
(**8**)	Anthraquinone	4.02	7.93
(**9**)	Anthraquinone	0.72	1.97
(**10**)	Methyl viologen	1.09	2.02
(**11**)	Methyl viologen	0.79	1.61

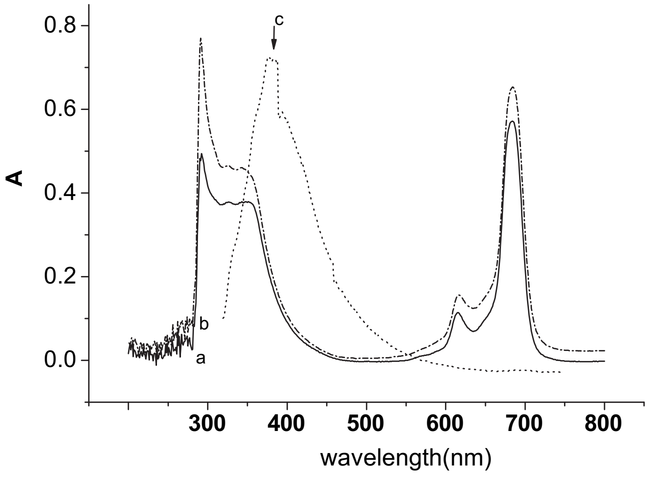


Fig. 5. Fluorescence spectra of (**8**) (a), (**9**) (b) and second generation alcohol (c) when they are excited at 290 nm.

anthraquinone, the fluorescence intensities were reduced. The data could be analyzed according to the Stern–Volmer equation (Eq. (1)) [21], where I_0 and I are the intensities of fluorescence in the absence and presence of the quencher respectively, [Q] is the concentration of the quencher, and K_{SV} is the Stern–Volmer quenching constant, which is the product of the bimolecular quenching rate constant (k_q) and the lifetime of the fluorescing species in the absence of the quencher (τ_S).

$$I_0/I = 1 + K_{SV}[Q] = 1 + k_q \tau_S [Q] \quad (1)$$

Fig. 3 showed the Stern–Volmer plots for (**8**)–(**9**) from which the values of K_{SV} and k_q could be determined (Table 2). The results showed that the value of K_{SV} is greater for lower generation dendrimers. This maybe due to the lower generation dendrimers provided a less hindered environment enabling the quencher to reach the vicinity of the phthalocyanine core. It could be concluded that the fluorescence was more effectively quenched in lower generation dendrimer compared with higher generation ones. As the quenching constant for (**9**) is still comparatively large, it appears that the four dendritic substituents are not bulky enough to form a globular structure. Since the fluorescence lifetime of anthraquinone is on the order of 10^{-8} s, the apparent quenching coefficients k_q for (**8**)–(**9**) are on the order of 10^{11} L mol^{-1} s^{-1}, about 1 order of magnitude higher than the normal value for dynamic quenching (ca. 10^{10} L mol^{-1} s^{-1} [22]). This may be related to the large encounter distance associated with the dendritic molecules.

The fluorescence intensities of (**10**)–(**11**) in water was also examined by *N*,*N*-dimethyl-γ,γ′-dipyridylium dichloride (methyl viologen, MV^{2+}) which acted as a cationic quencher (Fig. 4). The fluorescence intensities of these water-soluble phthalocyanines (**10**)–(**11**) were greatly quenched with an increasing amount of MV^{2+}. According to Stern–Volmer quenching equation, the value of K_{SV} was also greater for lower generation dendrimer. Since the fluorescence lifetime of MV^{2+} is of the order of 10^{-8} s, the apparent quenching coefficient K_q for (**10**)–(**11**) are of the order of 10^{11} L mol^{-1} s^{-1}, which is higher than the normal value for dynamic quenching. This strongly suggested that the fluorescence quenching of (**10**)–(**11**) by MV^{2+} was mainly through a static quenching mechanism. Furthermore, addition of NaCl drastically diminished the fluorescence quenching by MV^{2+}. These phenomena could be explained that the local concentration of MV^{2+} adjacent to the dendrimer surface decreased because of the competitive binding of the sodium ions. This efficient quenching of phthalocyanine fluorescence occurs via accumulation of MV^{2+} on the negatively charged dendrimer surface. The fluorescence quenching results suggested an electron transfer reaction between the zinc phthalocyanine and MV^{2+} through the dendrimer framework.

Besides these photoinduced intermolecular electron transfer processes, the photoinduced intramolecular energy transfer in (**8**)–(**9**) was also examined. The second generation alcohol exhibited absorption band at 290 nm in DMSO and an emission at

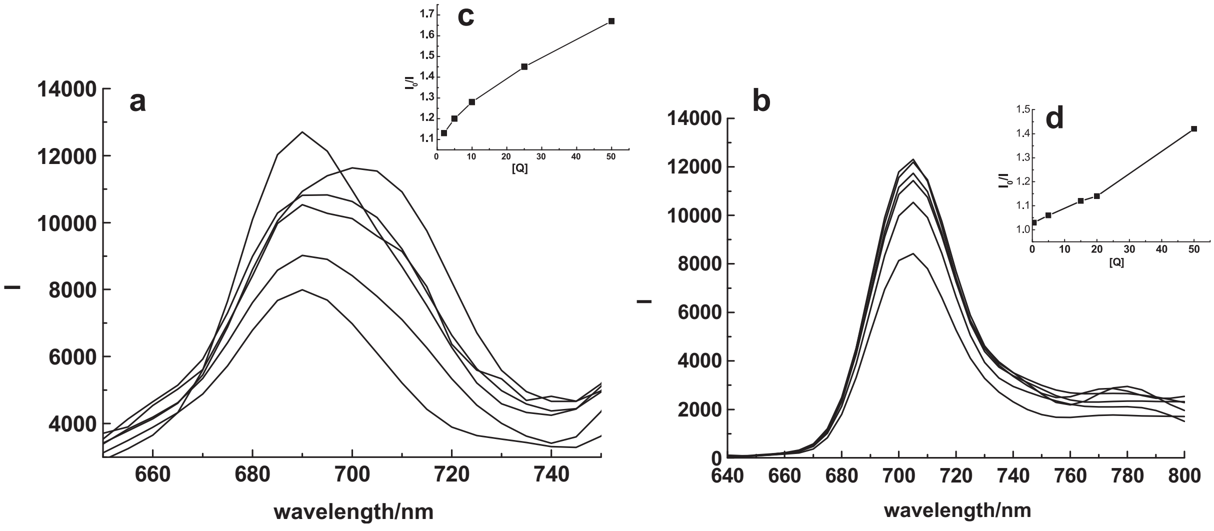


Fig. 4. Fluorescence spectra of (**10**) (a) and (**11**) (b) quenching by MV^{2+} in water. $c_{(10),(11)} = 2.0 \times 10^{-5}$ mol L^{-1} in all cases. $c_{MV2+} = (\times 10^{-5}$ mol L^{-1}) from up to down: 0, 2, 5, 10, 25, 50. Inset plots: Stern–Volmer plots for the fluorescence quenching of (**10**) (c) and (**11**) (d) in water by MV^{2+}.

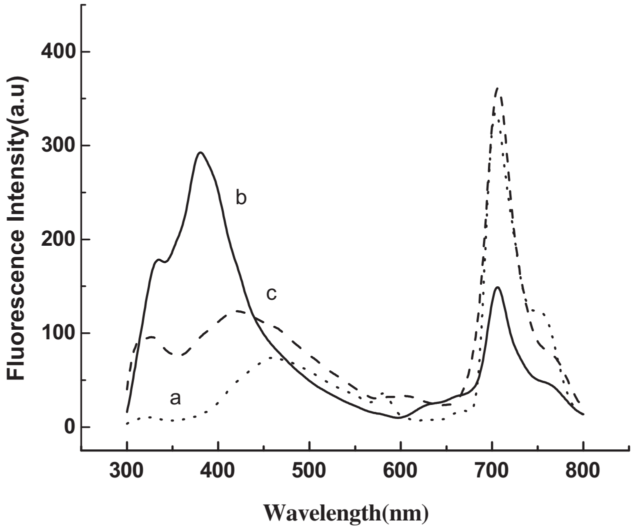


Fig. 6. Fluorescence spectra of (**8**) (b) and (**9**) (c) upon and tetrasulfonate zinc phthalocyanine (a) excitation at 290 nm in DMSO.

382–396 nm upon excitation at 290 nm. As the emission band was partially overlapped with the B bands of phthalocyanines, the dendritic subunits of (**8**)–(**9**) had a chance to transfer energy from the excited dendritic substitutions to the phthalocyanine core (Fig. 5). Upon excitation at 290 nm, where the absorption of phthalcyanines were weak, (**8**)–(**9**) emitted strongly at 420 nm due to the dendritic substitutions, together with an emission at 703 nm. For comparison, tetrasulfonate zinc (II) phthalocyanine, which does not contain aromatic dendritic substitutions, was studied upon excitation at 290 nm. It exhibited only an emission at 690 nm (Fig. 6). The former emission was obviously due to a singlet–singlet intramolecular energy transfer from the excited dendritic subunit to the central phthalocyanine core [23].

4. Conclusion

Two new series of zinc (II) phthalocyanines carrying four poly (aryl benzyl ether) dendritic substituents with terminal cyano and carboxylic acid functionalities have been synthesized and unambiguously characterized. These compounds mainly exhibited in monomeric form in both common organic solvent and water. They undergo photoinduced electron transfer with various quenchers and intramolecular energy transfer from the excited dendritic subunits to the phthalocyanines which acts as an energy trap. These photoproperties suggest that a new and efficient light-harvesting system can be developed based on dendritic phthalocyanine system.

Acknowledgment

This study was supported by the National Natural Science Foundation of China (No. 20604007), Natural Science Foundation of Fujian (Nos. 2008J0078, 2007F30103, 2009J01020), Key Foundation for Technology Department (No. 2007I0013) and Project WKJ2008-2-61 supported by the Science Research Foundation of Ministry of Health & United Fujian Provincial Health and Education project for Tackling the Key Research, China.

References

[1] Dolmans DE, Fukumura D, Jain RK. Photodynamic therapy for cancer. Nature Reviews Cancer 2003;3:380–7.

[2] Konan YN, Gurny R, Allemann E. State of the art in the delivery of photosensitizers for photodynamic therapy. Journal of Photochemistry and Photobiology B 2002;66:89–106.

[3] Gerhardt SA, Lewis JW, Kliger DS, Zhang JZ, Simonis U. Effect of micelles on oxygen-quenching processes of triplet-state para-substituted tetraphenylporphyrin photosensitizers. Journal of Physical Chemistry, A 2003;107 (15):2763–7.

[4] Lukyanets EA. Phthalocyanines as photosensitizers in the photodynamic therapy of cancer. Journal of Porphyrins and Phthalocyanines 1999;3(6-7): 424–32.

[5] Ng CH, Li X, Ng DKP. Synthesis and photophysical properties of nonaggregated phthalocyanines bearing dendritic substituents. Macromolecules 1999;32: 5292–8.

[6] Ng KPD. Dendritic phthalocyanines: synthesis, photophysical properties and aggregation behavior. Comptes Rendus Chimie 2003;6:903–10.

[7] Jang W, Nakagishi Y, Nishiyama N, Kawauchi S, Morimoto Y, Kikuchi M, et al. Polyion complex micelles for photodynamic therapy: incorporation of dendritic photosensitizer excitable at long wavelength relevant to improved tissue-penetrating property. Journal of Controlled Release 2006;113:73–9.

[8] Kimura M, Sugihara Y, Muto T, Hanabusa K, Shirai H, Kobayashi N. Dendritic metallophthalocyanines-synthesis, electrochemical properties, and catalytic activities. Chemistry – A European Journal 1999;5(12):3495–500.

[9] Kimura M, Nakada K, Yamaguchi Y, Hanabusa K, Shirai H, Kobayashi N. Dendritic metallophthalocyanines: synthesis and characterization of a zinc(II) phthalocyanine[8]^3-arborol. Chemical Communications; 1997:1215–6.

[10] Uchiyama T, Ishii K, Nonomura T, Kobayashi N, Isoda SA. Phthalocyanine dendrimer capable of forming spherical micelles. Chemistry – A European Journal 2003;9:5757–61.

[11] Brewis M, Helliwell M, McKeow NB. Phthalocyanine-centred aryl ether dendrimers with oligo(ethyleneoxy) surface groups. Tetrahedron Letters 2001;42:813–6.

[12] McKeown NB. Phthalocyanine-containing dendrimers. Advanced Materials 1999;11(1):67–9.

[13] Brewis M, Clarkson GJ, Goddard V, Helliwell M, Holder AM, McKeown NB. Silicon phthalocyanines with axial dendritic substituents. Angewandte Chemie International Edition 1998;37(8):1092–4.

[14] Leclaire J, Dagiral R, Fery-Forgues S, Coppel Y, Donnadieu B, Caminade A, et al. Octasubstituted metal-free phthalocyanine as core of phosphorus dendrimers: a probe for the properties of the internal structure. Journal of the American Chemical Society 2005;127:15762–70.

[15] Masakazu N, Atsuya M, Yoshihiro S, Yoshinobu N, Tatsuo A. Synthesis and photophysical properties of water-soluble dendrimers bearing a phthalocyanine core. Journal of Porphyrins and Phthalocyanines 2007;11(6):448–54.

[16] Hawker CJ, Frechet JM. Preparation of polymers with controlled molecular architecture. A new convergent approach to dendritic macromolecules. Journal of the American Chemical Society 1990;112:7638–47.

[17] Frechet JM. Functional polymers and dendrimers: reactivity, molecular architecture, and interfacial energy. Science 1994;263(5154):1710–5.

[18] Kaneko R, Jikei M, Kakimoto M. Preparation and properties of composite materials composed of hyperbranched aromatic polyamide and vinyl polymers. High Performance Polymers 2002;14:41–51.

[19] Peng Y, Huang F, Weng J, Huang B, Ma X. A spectroscopic study of the interaction of octacarboxylicmetal phthalocyanine with bovine serum albumin. Journal of Coordination Chemistry 2008;61(10):1503–12.

[20] Brasseur N, Langlois R, Madeleine CL, Ouellet R, Van Lier EJ. Receptor-mediated targeting of phthalocyanine to macrophages Via covalent coupling to native or maleylated bovine serum albumin. Photochemistry and Photobiology 1999;69(3):345–52.

[21] Filyasova AI, Kudelina IA, Feofanov AV. A spectroscopic study of the interaction of tetrasulfonated aluminum phthalocyanine with human serum albumin. Journal of Molecular Structure 2001;565-566:173–6.

[22] Dockal M, Carter DC, Rüker F. Conformational transitions of the three recombinant domains of human serum albumin depending on pH. Journal of Biological Chemistry 2000;275(5):3042–50.

[23] Devadoss C, Bharathi P, Moore JS. Energy transfer in dendritic macromolecules: molecular size effects and the role of an energy gradient. Journal of the American Chemical Society 1996;118:9635–44.