



Synthesis, structure and third-order optical nonlinearities of hyperbranched metal phthalocyanines containing imide units

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ABSTRACT

A series of thermally stable and soluble hyperbranched metal phthalocyanines oligomers containing imide units (HMePcIs) ending with carboxyl groups were synthesized successfully. The number of the Pc rings was first estimated by analyzing the terminal carboxyl groups in the ¹H NMR spectra of HMePcIs. The third-order nonlinear optical (NLO) properties of these oligomers were measured by a Z-scan technique with a pulsed Q-switched Nd:YAG laser system at 532 nm. The introduced imide unit noticeably improved the thermal stability and third-order nonlinear susceptibility, $\chi^{(3)}$. The 5 wt% weight loss temperature for HMePcIs exceeded 410 °C, and the $\chi^{(3)}$ values reached the order of 10^{-13} esu. The variation of the center metals of HMePcIs influenced the third-order optical nonlinearity, and the third-order nonlinear susceptibility $\chi^{(3)}$ values of hyperbranched metal (Zn, Cu, Ni) phthalocyanines oligomers were found to rank in the order of HZnPcI > HCuPcI > HNiPcI.

1. Introduction

Phthalocyanines (Pcs), containing an 18-electron conjugated macrocycle, have been extensively investigated in diverse fields, including dyes, catalysis, optical materials and so on, for the past several decades [1–9]. Among these Pcs, hyperbranched metal phthalocyanine (HMePc) oligomers polymerized from bis(3,4-dicyanobenzene) monomers with metal chloride have attracted extensive attention as high dielectric, electron transport and solar cell materials. Guo et al. synthesized novel organic HPcs with 1,2-bis(3,4-dicyanophenoxy)benzene for the first time, and the high dielectric research showed that the HPcs possessed impressive dielectric properties with very low loss at high operational frequencies [10]. Lee et al. introduced novel organic hyperbranched CuPc as a hole injection nanolayer on indium-tin oxide (ITO), and the layer dramatically improved the luminous efficiency and brightness of single-layer organic light-emitting diode (OLED) devices [11]. Li et al. synthesized a series of HPcs applied as TiO₂ sensitizers in semi-opaque dye sensitized solar cells with an improvement of efficiencies up to 1.15% [12].

Recently, phthalocyanine-based third-order nonlinear optical (NLO) devices have gained special attention for their large nonlinear susceptibility and fast response time [13–20]. Our previous report also

found that HPcs showed good third-order NLO properties, and the third-order nonlinear susceptibility, $\chi^{(3)}$, values of HPc oligomers could also be tuned by changing the central metals. HMePcs prepared using transition metals have more d orbital electrons and possess superior third-order NLO properties in the order of HCuPc > HNiPc > HCoPc [21].

The highly branched three-dimensional molecular structure provides these HMePcs with unique physical and chemical properties, such as good solubility and low solution viscosity for processing and application as well as a large conjugated structure for better electrical and optical properties. Although many HPcs have been synthesized, little attention has been paid to their preparation, structural analysis and terminal control. It is difficult to prepare hyperbranched zinc phthalocyanine (HZnPc) from bis(3,4-dicyanobenzene) with zinc chloride [22]. However, preparing HZnPcs is important for us to research the structures and properties of HMePcs. On the one hand, zinc in HMePc is different from paramagnetic copper, nickel and cobalt, which does not disturb nuclear magnetic resonance (NMR) signals, so the valuable ¹H NMR spectrum can be obtained to analyze the structure of HZnPc. On the other hand, zinc in HZnPc has more d orbital electrons, which provide better third-order NLO properties [21].

In this paper, we synthesized a series of novel hyperbranched metal

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phthalocyanines oligomers (HMePcIs) containing imide units for systematic study. The addition of imide units was adopted to improve the thermal properties and optical properties of the final HMePcIs [23–25]. We can obtain the carboxyl group terminated HZnPCIs directly by regulating and controlling the reaction conditions. The structures of the HZnPCIs were confirmed by ^1H NMR, and the phthalocyanine ring numbers of obtained HMePcIs were calculated for the first time. The relationships between the molecular weight and the phthalocyanine ring numbers of HZnPCIs were observed. Furthermore, the third-order NLO behaviors of HMePcIs and the effect of central metals (Zn, Cu and Ni) on the third-order nonlinear optical coefficient were systematically investigated.

2. Experiment

2.1. Materials

4,4'-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA), 1,2,4,5-Benzenetetra-carboxylic anhydride (PMDA), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), and 4,4'-Oxydiphthalic anhydride (ODPA) were purchased from Tokyo Chemical Industry and used without further purification. 4-Aminophthalonitrile (AR) was obtained from Alpha Chemicals Co. Ltd. and purified by recrystallizing it twice from water before use. Dimethyl sulfoxide (DMSO), *N,N*-Dimethylformamide (DMF) and *N,N*-dimethylacetamide (DMAc) were purified by distillation under reduced pressure over calcium hydride. All other chemicals, including acetic anhydride, pyridine, acetonitrile, ethanol, cuprous chloride, nickel dichloride, and ammonium molybdate, were obtained from commercial sources and used as described previously [21,25].

2.2. Instruments

IR spectra (KBr pellet) were recorded on a Nicolet Impact 410FTIR spectrophotometer. The ^1H NMR spectra were recorded on a Bruker 510 instrument with dimethylsulfoxide- d_6 (DMSO- d_6) as the solvent. UV–vis absorption spectra were recorded on a UV2501-PC spectrophotometer in DMF solution at room temperature. The monomer molecular weight was using a MALDI-TOF-MS (AXIMA-CFR) analyzer with DMF solution. Elemental analysis was performed on an Elemental Analyses MOD-1106 system. Gel permeation chromatograms (GPC) employing polystyrene as a standard were obtained with an Agilent PL-GPC220 instrument with *N,N*-dimethylformamide (DMF) as the eluent at a flow rate of 1 mL min^{-1} . Thermogravimetric analysis was performed using a Perkin–Elmer Pyris 1 TGA analyzer under a nitrogen atmosphere (200 mL min^{-1}) at a heating rate of $10\text{ }^\circ\text{C/min}$. The nonlinear optical properties of the oligomers were measured by a Top-hat Z-scan technique using a Q-switched Nd: YAG laser system with pulse width of 21 ps and frequency of 10 Hz at a wavelength of 532 nm. The sample solution was placed in a 2-mm-thick quartz cell and moved along the axis of the incident beam (z direction). The input energy was $0.51\text{ }\mu\text{J}$.

2.3. Synthesis of the monomers

The typical process for the preparation of monomer a is illustrated in Scheme 1. First, 4.29 g (30 mmol) of 4-aminophthalonitrile was dissolved in 35 mL of dry dimethylsulfoxide in a three-necked 250 mL flask with a nitrogen inlet, calcium chloride drying tube, and glass stopper. The solution was stirred with a magnetic bar. Dry nitrogen gas was bubbled through the solution, and then 6.66 g (15 mmol) of solid 6FDA was added to the vigorously stirred solution. After stirring for 0.5 h, a mixture of 20 mL of acetic anhydride/pyridine (5/4 v/v) was added, and the reaction mixture was stirred at $60\text{ }^\circ\text{C}$ for 10 h. After cooling to room temperature, the mixture was poured into a large amount of deionized water. The solid was collected and recrystallized

from acetonitrile. The yellow powdery product was dried in vacuum, affording 9.4 g of compound (a), yield: 85%, m/z : 625, IR (KBr, cm^{-1}): 3091, 2233, 1784, 1730, 1384, 1142, $721\text{ }^1\text{H}$ NMR (300 MHz, DMSO- d_6 , d, ppm): 8.333–8.361 (d, 2H, $J = 8.4\text{ Hz}$), 8.267–8.294 (d, 2H, $J = 8.1\text{ Hz}$), 8.215–8.221 (d, 2H, $J = 1.8\text{ Hz}$), 8.026–8.054 (d, 2H, $J = 8.4\text{ Hz}$), 8.020–8.048 (d, 2H, $J = 8.4\text{ Hz}$), 7.791 (s, 2H). Elem. Anal. Calcd for $\text{C}_{35}\text{H}_{12}\text{F}_6\text{N}_6\text{O}_4$: C 60.53%, H 1.74%, N 12.10%. Found: C 60.79%, H 1.83%, N 12.57%.

According to the above process, cyano-ended monomers with imide units b–e were synthesized.

For monomer b: yield: 83%, $m/z = 468$, IR (KBr, cm^{-1}): 3106, 2235, 1783, 1733, 1374, 1110, $723\text{ }^1\text{H}$ NMR (300 MHz, DMSO- d_6 , d, ppm): 8.565 (s,2H),8.369–8.397 (d, 2H, $J = 8.4\text{ Hz}$), 8.298–8.304 (d, 2H, $J = 1.8\text{ Hz}$),8.107–8.135 (d, 2H, $J = 8.4\text{ Hz}$), 8.100–8.129(d, 2H, $J = 8.7\text{ Hz}$). Elem. Anal. Calcd for $\text{C}_{26}\text{H}_8\text{N}_6\text{O}_4$: C 66.67%, H 1.72%, N 17.94%. Found: C 66.81%, H 1.81%, N 13.67%.

For monomer c: yield: 81%, $m/z = 548$, IR (KBr, cm^{-1}): 3072, 2233, 1778, 1727, 1374, 1078,738.1H NMR (300 MHz, DMSO- d_6 , d, ppm): 8.560 (s,2H),8.451–8.478 (d, 2H, $J = 8.1\text{ Hz}$), 8.348–8.376 (d, 2H, $J = 8.4\text{ Hz}$),8.297–8.304 (d,2H, $J = 2.1\text{ Hz}$), 8.168–8.194 (d, 2H, $J = 8.4\text{ Hz}$), 8.087–8.122 (dd, 2H, $J = 8.4\text{ Hz}$). Elem. Anal. Calcd for $\text{C}_{32}\text{H}_{12}\text{N}_6\text{O}_4$: C 70.59%, H 2.22%, N 14.44%. Found: C 70.80%, H 2.21%, N 14.67%.

For monomer d: yield: 75%, $m/z = 572$, IR (KBr, cm^{-1}): 3108, 2235, 1783, 1733, 1373, 1097, $723\text{ }^1\text{H}$ NMR (300 MHz, DMSO- d_6 , d, ppm): 8.347–8.375 (d, 2H, $J = 8.4\text{ Hz}$), 8.294–8.322(d,2H, $J = 8.4\text{ Hz}$), 8.280 (s, 2H), 8.255–8.284 (dd, 2H, $J = 8.7\text{ Hz}$),8.222–8.229 (d, 2H, $J = 2.1\text{ Hz}$), 8.070–8.106 (dd, 2H, $J = 8.7\text{ Hz}$). Elem. Anal. Calcd for $\text{C}_{33}\text{H}_{12}\text{N}_6\text{O}_5$: C 69.23%, H 2.11%, N 13.97%. Found: C 69.48%, H 2.16%, N 14.28%.

For monomer e: yield: 79%, $m/z = 564$, IR (KBr, cm^{-1}): 3091, 2233, 1779, 1727, 1373, 1081,740. ^1H NMR (300 MHz, DMSO- d_6 , d, ppm): 8.327–8.355 (d, 2H, $J = 8.4\text{ Hz}$), 8.144–8.174 (d, 2H, $J = 9.0\text{ Hz}$), 8.253–8.260 (d, 2H, $J = 2.1\text{ Hz}$), 8.042–8.078 (dd, 2H, $J = 8.4\text{ Hz}$), 7.687–8.717 (d, 2H, $J = 9.0\text{ Hz}$),7.711 (s,2H). Elem. Anal. Calcd for $\text{C}_{32}\text{H}_{12}\text{N}_6\text{O}_5$: C 68.57%, H 2.14%, N 14.99%. Found: C 68.72%, H 2.03%, N 15.09%. Mass spectrum data of monomer a–e (Figure S1–S5) are listed in the Supporting Information.

2.3.1. Synthesis of the hyperbranched metal phthalocyanines oligomers containing imide units (HMePcIs)

The typical process for the preparation of the HMePcIs oligomer is illustrated in Scheme 2. In a three-necked flask, 2.09 g (3 mmol) of monomer (a) and 0.186 g (1 mmol) of $\text{Zn}(\text{CH}_3\text{COO})_2$ were dissolved in 40 mL of DMAc with 0.3 g $(\text{NH}_4)_2\text{MoO}_4$. Then, the mixture was stirred at $160\text{ }^\circ\text{C}$ for 24 h under nitrogen. After cooling to room temperature, the reaction mixture was poured into 600 mL of deionized water. The crude product was first collected by filtration. Then, it was washed with deionized water and refluxed in acetonitrile twice. Finally, the product was filtered and rinsed with cold methanol. The obtained dark green powdery product was dried in vacuum, affording 1.5 g of hyperbranched zinc phthalocyanine (oligomer A). According to the above process, different carboxyl-ended oligomers B–E containing imide units were synthesized. Then, hyperbranched copper phthalocyanine (oligomer F) and hyperbranched nickel phthalocyanine (oligomer G) were synthesized using monomer a with the corresponding compounds of metal, CuCl and NiCl_2 . The yields of the hyperbranched metal phthalocyanines were all above 80%.

3. Results and discussions

3.1. Synthesis of cyano-ended monomers containing imide units

The cyano-ended monomers containing imide structures were synthesized by a conventional two-step procedure, including a ring-opening reaction to form amic acid and a chemical imidization, by

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