doi:10.1246/cl.2012.1012

Tetrabrominated Naphthalocyaninatozinc Complex with Terminal Carboxylate Functionalities

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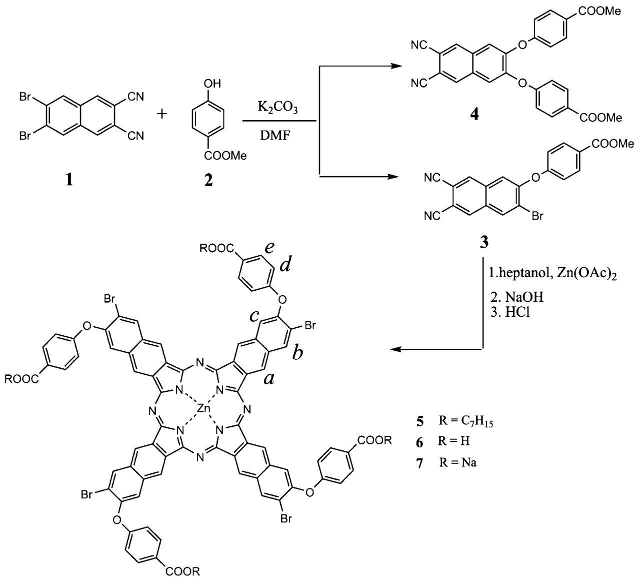
Novel hydrophilic naphthalocyanine was synthesized and characterized, which could be solublized in water as H-aggregates. It was found that this novel naphthalocyanine showed potential of application as optical limiting material.

Recently, naphthalocyanine (Nc) is of particular interest in optical materials for its expanded transmission window and red-shifted absorption compared to phthalocyanine (Pc).[1–7] The extension of the π-system results in Nc with remarkably high extinction coefficients in the near-infrared region, imparting superior photophysical properties to Nc. Among all nonlinear optical (NLO) materials that attract considerable studies at present,[8–12] Nc is one of the most promising optical limiters not only on the basis of its strong reverse saturable absorption (RSA) behavior and picosecond response time,[2,13,14] but also for its high thermal stability allowing harsh treatment for device process. On the other hand, it has been shown that Br-substituted Ncs exhibit better optical limiting properties than their counterparts, in which Br atoms are either on the peripheral of the macrocycle or as axial ligands.[15–17] However, there are fewer reports on Nc comparing to Pc, mainly because of its complicated synthetic procedures and poor solubility in common organic solvents.

As a matter of fact, the solubility of Nc is crucial during fabrication and deposition of this functional material into devices via solution-phase processability. Hence, the employment of substituents on Nc core allows for lowering its tendency to form stacked aggregates, while at the same time increasing its solubility in common organic solvents. Focusing on the structure–property–activity relationship, water-soluble moiety can be incorporated to endow Nc with hydrophilicity, thus enabling its processing under environmentally friendly conditions and fabrication of organic–inorganic materials to overcome the phase separation. To the best of our knowledge, few water-soluble Ncs have been reported so far.

Herein, we report the synthesis and characterization of novel tetrabrominated naphthalocyanine with terminal carboxylate functionalities. Scheme 1 shows the synthetic route used for the targeted zinc(II) naphthalocyanines.[33] Naphthalocyanine **5** was prepared starting from 6,7-dibromo-2,3-dicyanonaphthalene (**1**) that was synthesized following reported procedures.[4,18] Alkylation of **1** by commercially available methyl *p*-hydroxybenzoate (**2**) was asynchronous at the two adjacent Br atoms, with the monoalkylation product **3** predominating at 80 °C even in the presence of excess of **2**, in 74% yield. In comparison, the dialkylated product **4** was only formed at elevated temperatures. At 120 °C, using two equivalents of **2** to **1**, **4** was obtained in 15–20% yield accompanied by the monoalkylation product of **3**.



Scheme 1. Synthetic route for naphthalocyanine.

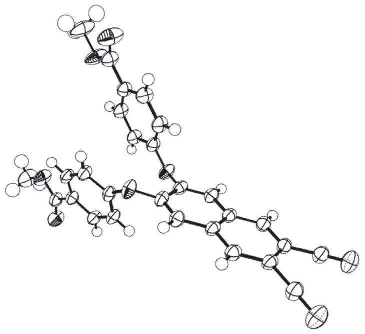


Figure 1. X-ray structure of **4**.

The molecular structure of **4** was established by single-crystal X-ray diffraction analysis. As shown in Figure 1, the two benzyl ester units are located at opposite sides of the dicyanonaphthalene plane. The dihedral angles formed by the dicyanonaphthalene ring and the benzene ring are 72.24(5) and 71.35(5)°, respectively.

Cyclization of **3** in the presence of zinc(II) acetate and a catalytic amount of DBU in *n*-heptanol at 160 °C led to the formation of Nc **5** with concomitant transesterification of the ester groups to give the corresponding heptyl esters; this has also been previously observed by us.[19,20] Due to its good solubility in

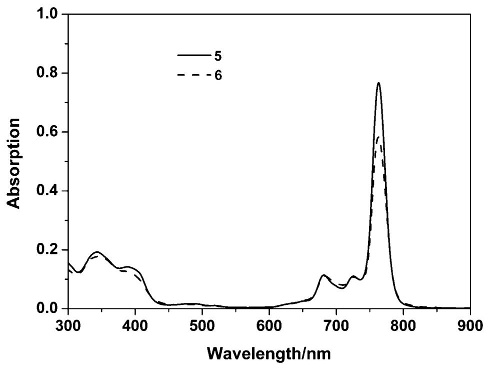


Figure 2. UV–vis absorption of **5** (solid, 2.20×10^{-6} M) and **6** (dash, 2.13×10^{-6} M) in DMF.

common organic solvents, **5** could be submitted to chromatographic purification using chloroform/pyridine (20:1) as eluent, which not only decreases the molecular aggregation but also reduces the adsorption of Nc on silica. Hydrolysis of the ester groups of **5** using NaOH in a mixed solvent system (THF/MeOH/H_2O), according to published procedure,[20] gave the Nc **7** bearing four sodium carboxylate groups. Upon addition of 1 M HCl to an aqueous solution of **7** until pH ≈3, a green precipitate of **6** was obtained in high yield. Compounds **5** and **6** are soluble in most organic solvents, such as THF, pyridine, DMF, $CHCl_3$, benzene, and DMSO, but show stronger tendency to aggregate in nonpolar solvents. In contrast, cyclization of **4** failed under the same conditions we used for formation of **5**; even at elevated temperature in trichlorobenzene, no corresponding Nc could be observed. The mass spectra (MALDI-TOF) of compounds **5** and **6** appeared at *m*/*z* 2029.97 (M^+) and 1636.96 (M^+) comparing to their theoretical *m*/*z* 2029.28 and 1636.84, respectively.

Both of **5** and **6** show similar UV–vis absorption upon dissolved in DMF as shown in Figure 2, with a highly resolved Q-band centered at 763 nm assigned to the monomeric species. The UV–vis spectra show almost no influence of peripheral chain length on their Q-band positions.

It is remarkable that compound **6** could be soluble in water. To date, no report can be found on the aggregation behavior of hydrophilic Nc in water yet, although a number of Pcs bearing hydrophilic moieties have been studied so far.[21–27] Original molecular aggregation studies of water-soluble Nc were conducted in solution as a function of increasing volume fraction of H_2O in H_2O–DMF solution of **6**. Upon increasing H_2O volume fraction (0 → 50%), aggregation of **6** was remarkably confirmed by a marked decrease in the Q band absorption at 763 nm with simultaneously rising of a hypsochromic peak at 710 nm (Figure 3), indicating that aggregation under these solvent conditions was predominantly cofical H-aggregation.

The thermal stabilities of these Ncs were evaluated by the thermogravimetric analysis of TG/DTA. Compounds **5** and **6** start to decompose directly at 305 and 311 °C, respectively, without melting points. These decompose temperatures indicate that such Nc derivatives are as highly thermally stable as Pcs.[28–32]

The nonlinear optical experiments were conducted on a Sunlight 200 ns Nd:YLF laser system as shown in Figure 4. The laser beam was divided into two beams: one was focused on the

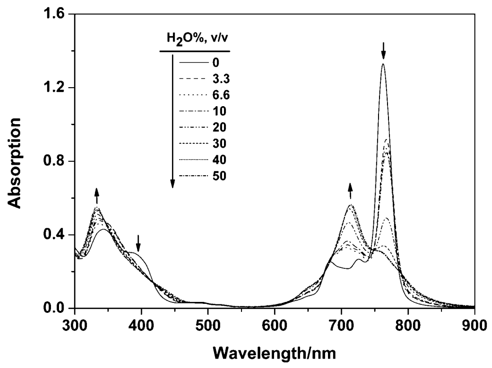


Figure 3. The electronic absorption spectra of **6** in DMF–H_2O mixed solvent with different volume ratios. The concentration of **6** was kept constant.

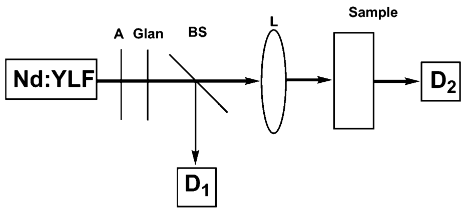


Figure 4. Experimental setup for optical limiting measurement. D_1 and D_2: reference and signal detectors; L: lens that focuses the laser onto the sample; BS: beam splitter; A: pinhole used to make the laser collimating; Glan: Glan prism that is used as a polarizer.

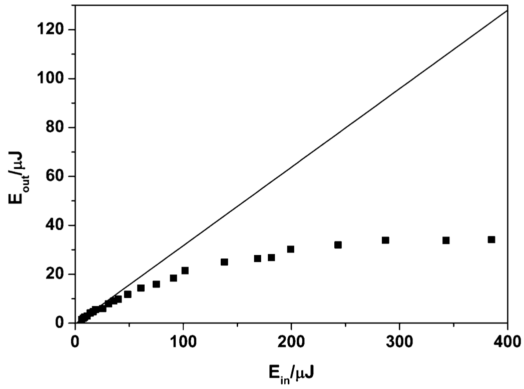


Figure 5. The optical-limiting properties **6** in DMF at the concentration of $[C] = 1 \times 10^{-2}$ M (cell thickness: 2 mm) upon excitation with 18 ns pulse at 1053 nm (The solid line gives the transmission if there were no limiting).

center of the sample cell, and the other was used as the reference beam. Nonlinear transmittance responses versus incident energy spanning from 25 to 400 μJ at 1053 nm with 18 ns pulse for Nc **6** in DMF ($[C] = 1 \times 10^{-2}$ M; cell thickness: 2 mm) are shown in Figure 5. The response of the Nc is linear to the input energy intensity at the beginning, but as input energy intensity increases, the transmittance of the solution decreases and a nonlinear relationship is observed between the output and input energy intensity, revealing the occurrence of reverse saturable absorption (RSA). The output energy of the limiter is restricted to 35 μJ for input energies over the range of our study, with less than 8% transmission as the incident energy is increased up to 400 µJ. The optical limiting threshold, which is defined as the input fluence at which the output transmittance is 50% of the linear transmittance is ca. 200 µJ for **6**. At energies that above the threshold, the ratio of the transmission of the Nc **6** limiter to that predicted by the linear line in Figure 5 is ca. 1/4.

In conclusion, novel hydrophilic tetrabrominated zinc(II) naphthalocyanine **6** has been successfully synthesized and characterized. This compound displays positive nonlinear optical absorption with a laser pulse. Obviously, this compound can further be applied to fabrication organic–inorganic hybrid materials to overcome the phase separation.

This work was supported by the grant from Natural Science Foundation of China (No. 21071090) and the Excellent Young Scientist Fund of Shandong Province (No. BS2010CL032). The authors also acknowledge the financial supports from the Research Fund for the Doctoral Program of Higher Education of China (No. 20100131120026).

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