Dyes and Pigments 99 (2013) 154–159

Contents lists available at SciVerse ScienceDirect

Dyes and Pigments

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

2,3,9,10,16,17,23,24-Octakis(phenoxy/octyloxy)phthalocyaninato manganese complexes. Synthesis, structure, and nonlinear optical property

Wei Sun [a], Hailong Wang [a], Junshan Sun [a], Jinglan Kan [a], Yanli Chen [b,**], Jianzhuang Jiang [a,*]

[a] Department of Chemistry, University of Science and Technology Beijing, Xueyuanlu 30, Beijing 100083, China
[b] School of Chemistry and Chemical Engineering, University of Jinan, Jinan 250022, China

ARTICLE INFO

Article history:
Received 14 March 2013
Received in revised form
20 April 2013
Accepted 23 April 2013
Available online 7 May 2013

Keywords:
Phthalocyanine
Manganese
Structure
Electrochemistry
Third order nonlinear optical property
Crystallography

ABSTRACT

2,3,9,10,16,17,23,24-Octakis(phenoxy)phthalocyaninato manganese complex MnCl[Pc(OPh)$_8$] (**1**) was prepared and spectroscopically and electrochemically characterized. For the comparative reason, 2,3,9,10,16,17,23,24-octakis(octyloxy) phthalocyaninato manganese analogue MnCl[Pc(OC$_8$H$_{17}$)$_8$] (**2**) was also prepared and comparatively studied. The molecular structure of **1** with a central chloridized trivalent manganese ion has been clearly determined by single-crystal X-ray diffraction analysis. The third order nonlinear optical properties of **1** and **2** in toluene solution were studied using *Z*-scan technique, giving effective imaginary third order molecular hyperpolarizability of 1.44×10^{-11} and 2.27×10^{-11} esu, respectively, indicating the potential application of the phthalocyaninato manganese complexes in the optical limiting.

1. Introduction

Phthalocyanines have been an important class of dyes and pigments with extensive applications in paint, printing, and textile industries ever [1]. Quite recently these macrocyclic molecular materials have also been important potential applications in the fields of organic field transistor (OFET) [2], photovoltaic cells [3], optical data storage [4], photosensitizers in the photodynamic therapy [5], nonlinear optics [6], gas sensors [7], organic photoconductors [8] due to their excellent spectroscopic, electrochemical, and photophysical properties. In particular, good nonlinear optical properties of some phthalocyaninato metal complexes revealed have stimulated great research interest in this field [9].

As early as in 1987, Ho and co-workers started to study the third-order NLO properties of phthalocyaninato complexes with the third main group metals including gallium and aluminum for the first time [10]. This was followed by the preliminary report of Coulter et al. on the optical limiting property of AlClPc in 1989 [11]. In the following two decades, quite a number of different kinds of phthalocyanine derivatives including the monomeric complexes of Pb, [12], Ni, [13], Co, [14], Cu, [14], Zn, [15], Si, [16], Ti, [17], V [18] and sandwich complexes of La, [19], Sm, [20,21], Eu, [15], and Gd [20] have been extensively studied for their third-order nonlinear optical properties with potential practical applications in optical limiting devices. Among which the phthalocyaninato indium/zinc complexes were revealed to show great potential due to their high effective imaginary third order molecular hyperpolarizability [22]. However, the design and synthesis of new phthalocyanine compounds with good NLO properties still attract increasing research interest in this field.

In the present paper, we describe the synthesis, spectroscopic, and electrochemical characterization of two new substituted phhtalocyaninato manganese complexes, namely 2,3,9,10,16,17,23,24-octakis(phenoxy) phthalocyaninato manganese complex MnCl[Pc(OPh)$_8$] (**1**) and 2,3,9,10,16,17,23,24-octakis(octyloxy) phthalocyaninato manganese MnCl[Pc(OC$_8$H$_{17}$)$_8$] (**2**). The molecular structure of MnCl[Pc(OPh)$_8$] (**1**) has been clearly clarified by single crystal X-ray

---

* Corresponding author. Tel.: +86 10 6233 2592.
** Corresponding author.
E-mail address: jianzhuang@ustb.edu.cn (J. Jiang).

0143-7208/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.dyepig.2013.04.029

diffraction analysis. In particular, good third order nonlinear optical property unraveled for both phthalocynato manganese compounds **1** and **2** in toluene solution reveals their potential application in the optical limiting field.

2. Experimental section

2.1. Materials and instruments

n-Pentanol and CH_2Cl_2 were distilled from sodium and anhydrous $CaCl_2$, respectively. Anhydrous 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) was purchased using Aldrich. 4,5-Di(phenoxy) phthalonitrile and 4,5-di(octyloxy)phthalonitrile were synthesized according to reported procedures [23,24]. Column chromatography was carried out on silica gel (Merck, Kieselgel 60, 200–300 mesh) with the indicated eluent. All other reagents and solvents were reagent grade and used as received.

The electronic absorption spectrum was obtained on Hitachi U-4100 spectrophotometer. IR spectrum (KBr pellets) was recorded on a BIORAD FTS-165 spectrometer. MALDI-TOF mass spectrum was recorded on a Bruker APEX47e ultra-high resolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with α-cyano-4-hydroxycinnamic acid as matrix. Elemental analysis was performed on an Elementar Vavio El III. Electrochemical measurement was carried out with a BAS CV-50W voltammetric analyzer. The cell comprised inlets for a glassy carbon disk working electrode of 2.0 mm in diameter and a silver-wire counter electrode. The reference electrode was Ag/Ag^+, which was connected to the solution by a Luggin capillary whose tip was placed close to the working electrode. It was corrected for junction potentials by being referenced internally to the ferrocenium/ferrocene (Fe^+/Fe) couple [$E_{1/2}$ (Fe^+/Fe) = 501 mV vs. SCE]. Typically, a 0.1 M solution of TBAP in CH_2Cl_2 containing 0.5 mM of sample was purged with nitrogen for 3 min, then the differential pulse voltammogram (DPV) was recorded at ambient temperature with the scan rate of 10 mV s^{-1}.

2.2. X-ray crystallography

Crystal data and details of data collection and structure refinement for **1** are given in Table 1. Data were collected on an Oxford Diffraction Gemini E system with an Mo-Kα sealed tube ($\lambda = 0.71073$ Å) at −150 °C, using a ω scan mode with an increment of 0.3°. Final unit cell parameters were derived by global refinements of reflections obtained from integration of all the frame data. The collected frames were integrated using the preliminary cell-orientation matrix. The SMART software was used for collecting frames of data, indexing reflections and determination of lattice constants; SAINT-PLUS for integration of intensity of reflections and scaling [25]; SADABS for absorption correction [26]; and SHELXL for space group and structure determination, refinements, graphics and structure reporting [27]. All the H atoms in these compounds were obtained geometrically. These H atoms were included in the subsequent least-squares refinement as fixed contributors. The final refinement with anisotropic temperature factors for non-H atoms led to *R* value of 0.0902 for **1**. The selected bond length and angle have been listed in Table S3 (Supporting Information). CCDC number of 921533 for **1**, containing the supplementary crystallographic data for this paper can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Table 1
Crystal data and structure refinements of MnCl[Pc(OPh)$_8$] (**1**).

Compound	**1**
Formula	$C_{80}H_{48}ClMnN_8O_8$
F.W.	1339.65
System	Triclinic
Space group	*P*-1
a	13.0939(7)
b	16.7585(16)
c	16.9423(17)
α	94.386(8)
β	95.593(6)
γ	95.105(6)
Z	2
Volume	3671.7(5)
D_{cald}/g cm^{-3}	1.212
F(000)	1380
R_1 $I > 2\theta$	0.0904
R_{w2} $I > 2\theta$	0.2620
R_1 all	0.1399
R_{w2} all	0.2947
S	1.039

2.3. Synthetic methods

2.3.1. Preparation of MnCl[Pc(OPh)$_8$] (1)

A mixture of 4,5-di(phenolxy)phthalonitrile (495 mg, 1.50 mmol), $Mn(OAc)_2 \cdot 4H_2O$ (92 mg, 0.38 mmol), and DBU (0.5 ml, 3.00 mmol) in *n*-pentanol (3 ml) was refluxed under a blanket of nitrogen for 6 h. The reaction mixture was allowed to cool in air and then methanol (80 ml) was added. The resulting solution was stirred for 10 min and filtered. The residue was washed with methanol and water and then dried. The crude product was purified by column chromatography with $CHCl_3$ and MeOH (10:3) as eluent and the brown band containing the MnCl[Pc(OPh)$_8$] (**1**) was collected. Repeated chromatography followed by recrystallization from $CHCl_3$ and MeOH gave pure target compound as a dark-brown powder with the yield of ca. 78%, 382 mg.

2.3.2. Preparation of MnCl[Pc(OC$_8$H$_{17}$)$_8$] (2)

By employing the above described procedure with 4,5-di(octyloxy)phthalonitrile (585 mg, 1.50 mmol) instead of 4,5-di(phenoxy)phthalonitrile as starting material, pure compound MnCl[Pc(OC$_8$H$_{17}$)$_8$] (**2**) was obtained as a dark-brown powder with the yield of ca. 89%, 533 mg.

3. Results and discussion

3.1. Synthesis and spectroscopic characterization

Cyclic tetramerization of corresponding phthalonitrile in the presence of manganese salt was usually employed for the preparation of unsubstituted phthalocyaninato manganese complex [28]. In addition to this widely employed method [29], substituted phthalocyaninato manganese complexes could also be prepared by direct insertion of metal ion into the central hole of corresponding metal free phthalocyanines [30]. Despite the synthesis of a few substituted phthalocyaninato manganese compounds with eight peripheral substituents, substituted phthalocyaninato manganese complex with eight phenoxy moieties at the peripheral position of phthalocyanine ligand has not been reported thus far. In the present case, cyclic tetramerization of 4,5-di(phenoxy) phthalonitrile in the presence of $Mn(OAc)_2 \cdot 4H_2O$ promoted by organic base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in refluxing *n*-pentanol followed by the treatment with a large amount of chloridized organic solvent like $CHCl_3$ led to the isolation of 2,3,9,10,16,17,23,24-octakis(phenoxy) phthalocyaninato manganese MnCl[Pc(OPh)$_8$] (**1**). For the comparative studies, 2,3,9,10,16,17,23,24-octakis(octyloxy) phthalocyaninato manganese analogue MnCl[Pc(OC$_8$H$_{17}$)$_8$]

(**2**) was also prepared by employing the same procedure with 4,5-di(octyloxy)phthalonitrile instead of 4,5-di(phenoxy)phthalonitrile as starting material. Satisfactory elemental analysis results were obtained for the two newly prepared complexes **1** and **2** after repeatedly column chromatography followed by recrystallization. Both compounds were also characterized with a range of spectroscopic methods. The MALDI-TOF mass spectrum of **1** showed an intense cluster corresponding to the molecular ion $(M)^+$, Fig. S1a (Supporting Information). This is also true for the analogue **2**, Fig. S1b (Supporting Information).

The electronic absorption spectrum of MnCl[Pc(OPh)$_8$] (**1**) and MnCl[Pc(OC$_8$H$_{17}$)$_8$] (**2**) were recorded in $CHCl_3$ and shown in Fig. 1a and b, respectively. As can be found, both compounds display typical feature of the monomeric phthalocyaninato metal complexes in the electronic absorption spectra, revealing the nonaggregated molecular spectroscopic nature of **1** and **2** in $CHCl_3$. As shown in Fig. 1, the absorption at 392 and 391 nm with medium intensity is attributed to the phthalocyanine Soret band and the intense one at 730 and 729 nm with a shoulder at 657 and 655 nm to the phthalocyanine Q band. While the absorption at 518 and 504 nm is obviously associated with the ligand-to-metal charge transfer band [30(a),31] together with some contribution from the n → π* transition arising from the oxygen lone pairs of electrons [32].

Vibrational spectroscopy is a versatile technique for revealing the intrinsic properties of phthalocyanine compounds [33]. In the IR spectra of **1** and **2**, Fig. S2 (Supporting Information), in addition to the absorptions contributed from the central aromatic Pc macrocycle including the wagging and torsion vibrations of C–H groups, isoindole ring stretching vibrations, and the C═N aza group stretching vibrations [34], the asymmetric and symmetric C–O–C stretching for these compound **1** and **2** is observed at 1281 and 1086 cm^{-1} and 1279 and 1096 cm^{-1}, respectively, Fig. S2 (Supporting Information) [35]. The most intense bands observed at 2924–2926 and 2955–2958 cm^{-1} for **2**, which are absent in the IR spectrum of **1**, are due to the antisymmetric C–H stretching vibrations of the –CH$_2$– and –CH$_3$ groups, respectively, of the octyloxy side chains.

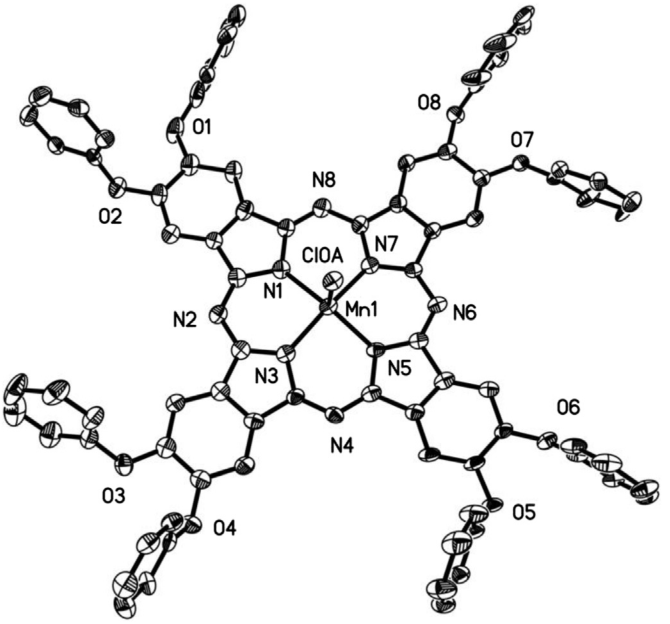

Fig. 2. Molecular structure of MnCl[Pc(OPh)$_8$] (1) in top view with the 30% probability thermal ellipsoids for all non-hydrogen atoms. All hydrogen atoms and solvent molecules are omitted for clarity.

3.2. *Structure of MnCl[Pc(OPh)$_8$] (1)*

Single crystals of MnCl[Pc(OPh)$_8$] (**1**) suitable for X-ray diffraction analysis were obtained by slow diffusion of *n*-hexane onto a $CHCl_3$ solution of this compound. This compound crystallizes in the triclinic system with a *P*-1 space group containing two molecules in each unit cell. Fig. 2 shows the molecular structure of MnCl [Pc(OPh)$_8$] (**1**). The five-coordinated manganese (III) ion locates in the center of phthalocyanine ring coordinated by four isoindole N atoms and one Cl atom, showing a tetragonal pyramid coordination geometry for the manganese (III) ion. As a consequence, the phthalocyanine chromophore in MnCl[Pc(OPh)$_8$] adopts conformation that is slightly domed toward the manganese (III) ion with a distance of 0.292 Å from the N$_4$ mean plane. In addition, the eight phenoxy moieties attached on the peripheral positions of phthalocyanine ring locates on the same side of the chloride atom most probably due to the steric hindrance of the phenoxy groups of the neighboring molecule.

Interestingly, two molecules of MnCl[Pc(OPh)$_8$] are bound together *via* π•••π stacking between the phthalocyanine ring, forming a dimeric supramolecular structure with phthalocyanine–phthalocyanine N4 planes separation distance of 3.386 Å. This as the basic building block further packs into a 2-D supramolecular structure *via* π•••π interaction between the phenyl π moieties of neighboring dimmers with the phenyl–phenyl distance of 4.153 Å. At the end this section, it is worth noting that efforts paid thus far still failed to lead to single crystals of MnCl[Pc(OC$_8$H$_{17}$)$_8$] (**2**), show in Fig. 3.

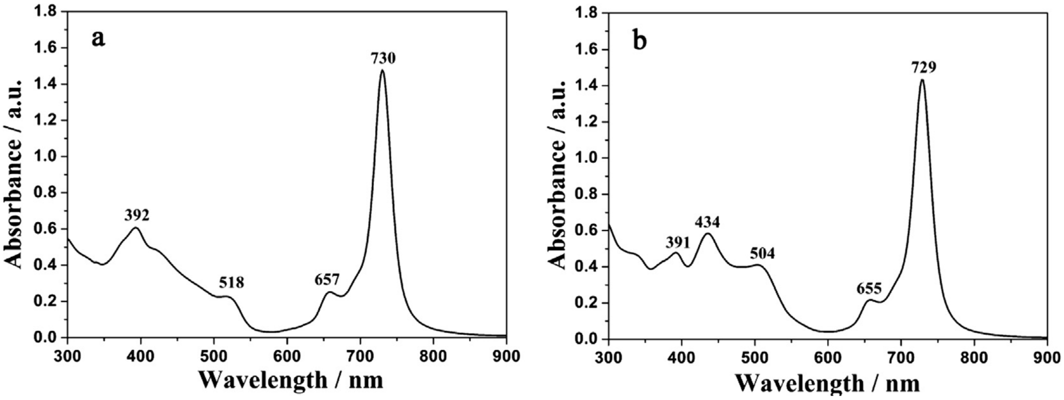

Fig. 1. Electronic absorption spectra of (a) MnCl[Pc(OPh)$_8$] (**1**) and (b) MnCl[Pc(OC$_8$H$_{17}$)$_8$] (**2**) in $CHCl_3$.

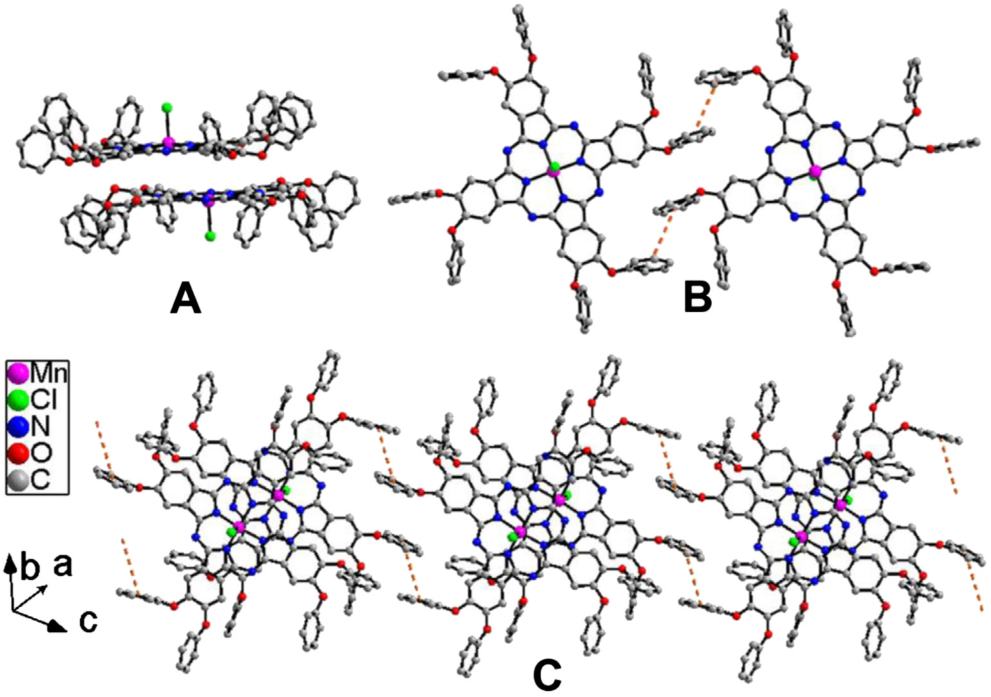

Fig. 3. The dimeric supramolecular structure of MnCl[Pc(OPh)$_8$] (**1**) by face-to-face $\pi\cdots\pi$ stacking interaction in top view (A), in side view (B) and 2-D supramolecular structure (C) with all hydrogen atoms and solvent molecules omitted for clarity.

*3.3. Electrochemistry of MnCl[Pc(OPh)$_8$] (**1**) and MnCl[Pc(OC$_8$H$_{17}$)$_8$] (**2**)*

The electrochemical behavior of both MnCl[Pc(OPh)$_8$] (**1**) and MnCl[Pc(OC$_8$H$_{17}$)$_8$] (**2**) complexes were studied by differential pulse voltammetry (DPV) in CH$_2$Cl$_2$. As shown in Fig. 4, compound **1** exhibited totally three quasi-reversible one-electron redox processes. The one at +1.02 V is attributed to the phthalocyanine ring-based oxidation of trivalent manganese complex MnCl[Pc(OPh)$_8$], while the quasi-reversible process at −0.97 V is due to the metal-based redox between Mn(II)/Mn(I) species. As a consequence, the one at −0.11 V is attributed to the metal-based redox between Mn(III)/Mn(II) [36]. This is also true for the analogous complex **2**. However, introduction of electron-donating octyloxy instead of electron-withdrawing phenoxy groups in this compound induces obvious shift of the three quasi-reversible one-electron redox processes to negative direction with phthalocyanine ring-based oxidation of trivalent manganese complex **2** at +0.84 V, the metal-based redox process between divalent manganese to trivalent manganese species at −1.12 V, and the phthalocyanine ring-based reduction of divalent manganese species at −0.47 V.

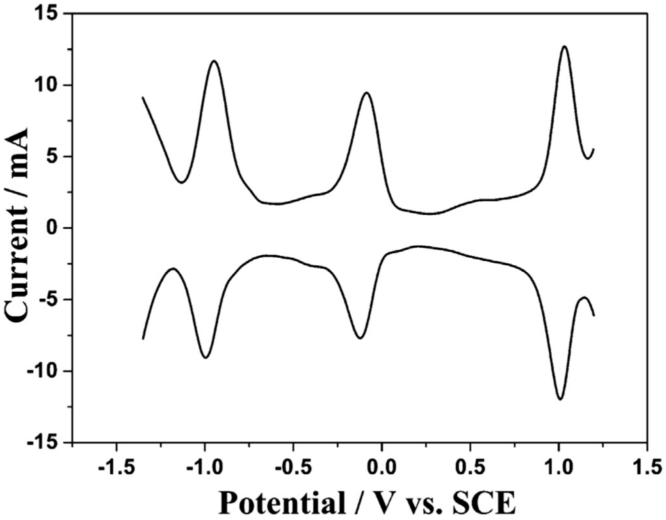

Fig. 4. Differential pulse voltammogram (DPV) of MnCl[Pc(OPh)$_8$] (**1**) recorded in CH$_2$Cl$_2$ containing 0.1 M TBAP at the scan rate of 10 mV s^{-1}.

3.4. Nonlinear optical property

The third order nonlinear optical property of MnCl[Pc(OPh)$_8$] (**1**) and MnCl[Pc(OC$_8$H$_{17}$)$_8$] (**2**) in toluene solution with the concentration of 1×10^{-3} M was studied using Z-scan technique with Nd-YAG laser as light source (the pulse width of 5 ns and wavelength of 532 nm). As exhibited in Fig. 5a, compound **1** in toluene solution shows reverse saturation absorption (RSA) under an open-aperture configuration mainly due to the thermal-induced nonlinear optical effect. The decreased transmission along with the increase in the incident energy indicates the potential optical limiting application of **1** and **2**. According to previously reported formula [37], the effective imaginary third order molecular hyperpolarizability (Im{$\chi^{(3)}$}) associated with the nonlinear refractive component of the phthalocyanine compound could be obtained by dividing the normalized Z-scanning data obtained under the open aperture configuration, giving the value of (Im{$\chi^{(3)}$}) being 1.44×10^{-11} esu for the solution sample. The comparable RSA value revealed for this phthalocyaninato manganese complex with other indium/zinc complexes of phthalocyanines or their hybrid materials with C$_{60}$ indicates its good potential of this compound as optical limiting material [22]. This is also true for the octakis(octyloxy)-substituted analogue MnCl [Pc(OC$_8$H$_{17}$)$_8$] (**2**) with the similar electronic molecular structure and therefore effective imaginary third order molecular hyperpolarizability of 2.27×10^{-11} esu, Fig. 5b.

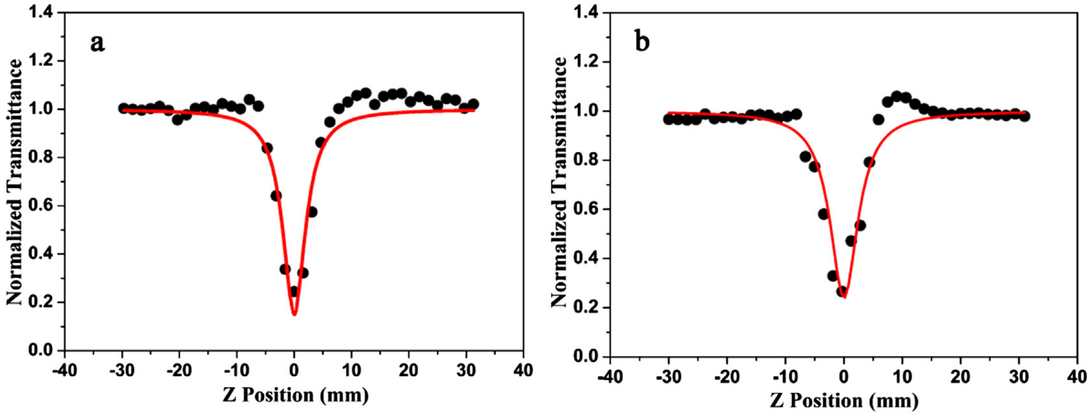

Fig. 5. Nonlinear optical property of (a) $\mathrm{MnCl[Pc(OPh)_8]}$ (1) and (b) $\mathrm{MnCl[Pc(OC_8H_{17})_8]}$ (2) in toluene solution under an open-aperture configuration.

4. Conclusion

Briefly summarizing above, two new peripherally octakis-(phenoxy)-substituted phthalocyaninato manganese complex has been synthesized and structurally characterized. The molecular structure of 2,3,9,10,16,17,23,24-octakis(phenoxy) phthalocyaninato manganese complex has been clearly revealed on the basis of single crystal X-ray diffraction analysis. In particular, good third order nonlinear optical property revealed for these phthalocyaninato manganese complexes in toluene solution suggests the potential applications of the phthalocyaninato manganese compounds in optical limiting field and will inspire research interest in this direction.

Acknowledgments

Financial support from the National Key Basic Research Program of China (Grant Nos. 2013CB933402 and 2012CB224801), Natural Science Foundation of China, Beijing Municipal Commission of Education, and University of Science and Technology Beijing is gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2013.04.029.

References

[1] (a) Berezin BD. Coordination compounds of porphyrins and phthalocyanines. New York: Wiley & Sons; 1981;
(b) Lever ABP, Leznoff CC. Phthalocyanine: properties and applications, vols. 1–4. New York: Wiley–VCH; 1989–1996;
(c) McKeown NB. Phthalocyanines materials: synthesis, structure and function. New York: Cambridge University Press; 1998;
(d) Kadish KM, Smith KM, Guilard R. The porphyrin handbook, vols. 1–20. San Diego, CA: Academic Press; 2000–2003;
(e) Advances in functional phthalocyanine materials. In: Jiang JJ, editor. Mingos DMP, Series Ed., editor. Structure and bonding, vol. 135. Heidelberg: Springer–Verlag; 2010.
[2] (a) Chen YL, Su W, Bai M, Jiang JJ, Li XY, Liu Y, et al. High performance organic field-effect transistors based on amphiphilic tris(phthalocyaninato) rare earth triple-decker complexes. J Am Chem Soc 2005;127:15700–1;
(b) Gao YN, Ma P, Chen YL, Zhang Y, Bian YZ, Li XY, et al. Design, Synthesis, characterization, and OFET properties of amphiphilic heteroleptic tris(phthalocyaninato) europium(III) complexes. The effect of crown ether hydrophilic substituents. Inorg Chem 2009;48:45–54;
(c) Kan JL, Chen YL, Qi DD, Liu YQ, Jiang JJ. High-performance air-stable ambipolar organic field-effect transistor based on tris(phthalocyaninato) europium(III). Adv Mater 2012;24:1755–8.
[3] (a) Jiao CJ, Zu NN, Huang KW, Wang P, Wu JS. Perylene anhydride fused porphyrins as near-infrared sensitizers for dye-sensitized solar cells. Org Lett 2011;13:3652–5;
(b) Ikda T, Aratani N, Osuka A. Synthesis of extremely π-extended porphyrin tapes from hybrid meso–meso linked porphyrin arrays: an approach towards the conjugation length. J Chem Asian 2009;4:1248–51;
(c) Wang Q, Li Y, Yan XZ, Ropp M, Galipeau D, Jiang JJ. Organic photovoltaic cells made from sandwich-type rare earth phthalocyaninato double and triple deckers. Appl Phys.Lett 2008;93:073303.
[4] Liu ZM, Yasseri AA, Lindsey JS, Bocian DF. Molecular memories that survive silicon device processing and real-world operation. Science 2003;302:1543–5.
[5] (a) LukCentyanets EA. Azaphthalocyanines with extended conjugation through heteroaryl and aryl substituents: photochemical and photophysical properties. J Porphyrins Phthalocyanines 1999;3:424–7;
(b) Ali H, van Lier JE. Metal complexes as photo- and radiosensitizers. Chem Rev 1999;99:2379–450.
[6] (a) Torre G, Vázquez P, Agullo-Lopez F, Torres T. Role of structural factors in the nonlinear optical properties of phthalocyanines and related compounds. Chem Rev 2004;104:3723–50;
(b) Senge MO, Fazekas M, Notaras EGA, Blau WJ, Zawadzka M, Locos OB, et al. Nonlinear optical properties of porphyrins. Adv Mater 2007;19:2737–74.
[7] (a) Chen YL, Bouvet M, Sizun T, Gao YN, Plassard C, Lesnie-wskac E, et al. Facile approaches to build ordered amphiphilic tris(phthalocyaninato) europium triple-decker complex thin films and their comparative performances in ozone sensing. Phys Chem Chem Phys 2010;12:12851–61;
(b) Bouvet M, Xiong H, Parra V. Molecular semiconductor-doped insulator (MSDI) heterojunctions: oligothiophene/bisphtalocyanine (LuPc2) and perylene/bisphthalocyanine as new structures for gas sensing. Sens Actuators B 2010;145:501–6.
[8] Zhou SQ, Qiu WF, Hu WP, Liu YQ, Bai FL, Zhu DB. Photoconduction and application of oxotitanium phthalocyanine dual-layered thin films. Thin Solid Films 2000;375:263–6.
[9] (a) Shirk JS, Pong RGS, Flom SR, Heckmann H, Hanack M. Effect of axial substitution on the optical limiting properties of indium phthalocyanines. J Phys Chem A 2000;104:1438–49;
(b) Heckmann H. Ph. D. thesis. Germany: University of Tübingen; 1999.
[10] Ho ZZ, Ju CY, Hetherington III WM. Third harmonic generation in phthalocyanines. J Appl Phys 1987;62:716–8.
[11] Coulter DR, Miskowski VM, Perry JW, Wei TH, Van Stryland EW, Hagan DJ. Optical limiting in solutions of metallo-phthalocyanines and naphthalocyanines. Spie Proc 1989;1105:42–6.
[12] James SS, Lindle JR, Bartoli FJ, Hoffman CA, Zakya HK, Arthur WS. Off-resonant third-order optical nonlinearities of metal-substituted phthalocyanines. Appl Phys Lett 1989;55:1287–9.
[13] Qu SL, Gao YC, Zhao CJ, Wang YX, Fu SY, Song YG, et al. Optical limiting properties in phthalocyanines with different substituent groups. Chem Phys Lett 2003;367:767–70.
[14] Calvete M, Yang GY, Hanack M. Porphyrins and phthalocyanines as materials for optical limiting. Synth Met 2004;141:231–43.
[15] Unnikrishnan KP, Thomas J, Nampoori VPN, Vallabhan CPG. Second hyperpolarizability of certain phthalocyanines and naphthalocyanines. Synth Met 2003;139:371–5.
[16] Liu MO, Tai CH, Sain MZ, Hu AT, Chou FI. Photodynamic applications of phthalocyanines. J Photochem Photobiol A 2004;165:131–6.
[17] O'Flaherty SM, Hold SV, Cook MJ, Torres T, Chen Y, Hanack M, et al. Molecular engineering of peripherally and axially modified phthalocyanines for optical limiting and nonlinear optics. Adv Mater 2003;15:19–21.
[18] Fang SL, Tada H, Mashiko S. Enhancement of the third-order nonlinear optical susceptibility in epitaxial vanadyl-phthalocyanine films grown on KBr. Appl Phys Lett 1996;69:767–9.
[19] Nalwa HS, Shirk JS. In: Leznoff CC, Lever ABP, editors. Phthalocyanines: properties and applications, vol. 4. New York: VCH Publishers, Inc.; 1996. p. 83.
[20] Mckeown NB. Dunn B, Goodby JW, West AR, editors. Phthalocyanine materials: synthesis, structure and function. Cambridge University Press; 1998.

[21] (a) Wang HL, Qi DD, Xie Z, Cao W, Wang K, Shang H, et al. A sandwich-type phthalocyaninato metal sextuple-decker complex: synthesis and NLO properties. Chem Commun 2013;49:889–91;
(b) Shang H, Wang HL, Wang K, Kan JL, Cao W, Jiang JJ. Sandwich-type tetrakis(phthalocyaninato) rare earth(III)-cadmium(II) quadruple-deckers. The effect of f-electrons. Dalton Trans 2013;42:1109–15.

[22] (a) He N, Chen Y, Bai J, Wang J, Blau WJ, Zhu J. Preparation and optical limiting properties of multiwalled carbon nanotubes with π-conjugated metal-free phthalocyanine moieties. J Phys Chem C 2009;113:13029–35;
(b) Kuang L, Chen QY, Sargent EH, Wang ZY. [60]Fullerene-containing polyurethane films with large ultrafast nonresonant third-order nonlinearity at telecommunication wavelengths. J Am Chem Soc 2003;125:13648–9;
(c) Manaa H, Tuhl A, Samuel J, AL-Mulla A, AL-Awadi NA, Makhseed S. Photophysical and nonlinear optical properties of zincphthalocyanines with peripheral substitutions. Opt Commun 2011;284:450–4.

[23] Tau P, Nyokong T. Electrochemical characterisation of tetra- and octa-substituted oxo(phthalocyaninato)titanium(IV) complexes. Electrochem Acta 2007;52:3641–50.

[24] Liu W, Jiang JJ, Pan N, Arnold DP. Heteroleptic phthalocyaninato-[2,3,9,10,16,17,23,24-octakis(octyloxy)phthalocyaninato] rare earth(III) triple-deckers: synthesis and spectroscopic characterization. Inorg Chem Acta 2000;310:140–6.

[25] SMART and SAINT for Windows NT software reference manuals, version 5.0. Madison, WI: Bruker Analytical X-Ray Systems; 1997.

[26] Sheldrick GM. SADABS – a software for empirical absorption correction. Germany: University of Göttingen; 1997.

[27] SHELXL reference manual, version 5.1. Madison, WI: Bruker Analytical X-Ray Systems; 1997.

[28] Torre GDL, Claessens G, Torres T. Phthalocyanines: old dyes, new materials. Putting color in nanotechnology. Chem Commun 2007;20:2000–15.

[29] (a) Trobach N, Hild O, Schettwein D, Wöhrle D. Synthesis and electropolymerisation of pyrrol-1-yl substituted phthalocyanines. J Mater Chem 2002;12:879–85;
(b) Wöhrle D, Eskes M, Shigehara K, Yamada A. A simple synthesis of 4,5-disubstituted 1,2-dicyanobenzenes and 2,3,9,10,16,17,23,24-octasubstituted phthalocyanines. Synthesis 1993:194–6;
(c) Idowu M, Nyokong T. Synthesis, photophysical and photochemical studies of water soluble cationic zinc phthalocyanine derivatives. Polyhedron 2009;28:416–24;
(d) Bayur ZA. Synthesis and characterization of novel soluble octa-cationic phthalocyanines. Dyes Pigm 2005;65:235–42.

[30] (a) Liu W, Lee CH, Chan HS, Mak TCW, Ng DKP. Synthesis, spectroscopic properties, and structure of [tetrakis(2,4-dimethyl-3-pentyloxy)phthalocyaninato]metal complexes. Eur J Inrog Chem 2004:286–92;
(b) Sehlotho N, Nyokong T. Effects of ring substituents on electrocatalytic activity of manganese phthalocyanines towards the reduction of molecular oxygen. J Electroanal Chem 2006;595:161–3.

[31] Stillman MJ, Nyokong T. In: Leznoff CC, Lever ABP, editors. Phthalocyanines: properties and applications, vol. 1. New York: VCH; 1989 [chapter 3].

[32] (a) Sheng N, Li RJ, Choi CF, Su W, Ng DK, Cui XG, et al. Heteroleptic bis(phthalocyaninato) europium(III) complexes fused with different numbers of 15-crown-5 moieties. Synthesis, spectroscopy, electrochemistry, and supramolecular structure. Inorg Chem 2006;45:3794–802;
(b) Zhang YX, Zhang XX, Liu ZQ, Bian YZ, Jiang JJ. Structures and properties of 1,8,15,22-tetrasubstituted phthalocyaninato-lead complexes: the substitutional effect study based on density functional theory calculations. J Phys Chem A 2005;109:6363–70.

[33] Jiang JJ, Bao M, Rintoul L, Arnold DP. Vibrational spectroscopy of phthalocyanine and naphthalocyanine in sandwich-type (na)phthalocyaninato and porphyrinato rare earth complexes. Coord Chem Rev 2006;250:424–48.

[34] (a) Jiang JJ, Arnold DP, Yu H. Infra-red spectra of phthalocyanine and naphthalocyanine in sandwich-type (na)phthalocyaninato and porphyrinato rare earth complexes. Polyhedron 1999;18:2129–39;
(b) Sun X, Bao M, Pan N, Cui X, Arnold DP, Jiang JJ. Infrared Spectra of phthalocyanine and naphthalocyanine in sandwich-type (na)phthalocyaninato and porphyrinato rare-earth complexes. II. The effects of rare-earth ionic size on the IR characteristics of naphthalocyanine in bis(naphthalocyaninato) rare-earth complexes. Aust J Chem 2002;55:587–95;
(c) Lu FL, Bao M, Ma CQ, Zhang XX, Arnold DP, Jiang JJ. Infrared spectra of phthalocyanine and naphthalocyanine in sandwich-type (na)phthalocyaninato and porphyrinato rare earth complexes. Part 3. The effects of substituents and molecular symmetry on the infrared characteristics of phthalocyanine in bis(phthalocyaninato) rare earth complexes. Spectrochim Acta A 2003;59:3273–86;
(d) Bao M, Pan N, Ma CQ, Arnold DP, Jiang JJ. Infrared spectra of phthalocyanine and naphthalocyanine in sandwich-type (na)phthalocyaninato and porphyrinato rare earth complexes: part 4. The infrared characteristics of phthalocyanine in heteroleptic tris(phthalocyaninato) rare earth complexes. Vibr Spectrosc 2003;32:175–84;
(e) Bao M, Bian YZ, Rintoul L, Wang RM, Arnold DP, Jiang JJ. Vibrational spectroscopy of phthalocyanine and naphthalocyanine in sandwich-type (na) phthalocyaninato and porphyrinato rare earth complexes: (part 10) the infrared and Raman characteristics of phthalocyanine in heteroleptic bis(phthalocyaninato) rare earth complexes with decreased molecular symmetry. Vibr Spectrosc 2004;34:283–91;
(f) Su W, Bao M, Jiang JJ. Infrared spectra of phthalocyanine and naphthalocyanine in sandwich-type (na)phthalocyaninato and porphyrinato rare earth complexes: part 12. The infrared characteristics of phthalocyanine in heteroleptic bis(phthalocyaninato) rare earth complexes. Vibr Spectrosc 2005;39:186–90.

[35] (a) Bai Z, Gao Y, Zhu P, Bian Y, Jiang J. Inorg Chem 2010;49:9005–11;
(b) Ogunbayo TB, Nyokong T. Photophysical and photochemical properties of Ni(II), Pd(II) and Pt(II) aryloxo and alkylthio derivatised phthalocyanine. J Mol Struct 2010;973:96–103.

[36] Lever ABP, Milaeva ER, Speier G. In: Leznoff CC, Lever ABP, editors. Phthalocyanines: properties and applications, vol. 3. New York: VCH Publishers; 1993. p. 1.

[37] Schmidt-Mende L, Fechtenkötter A, Müllen K, Moons E, Friend RH, Mackenzie JD. Self-organized discotic liquid crystals for high-efficiency organic photovoltaics. Science 2001;293:1119–22.