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Monophthalocyanine complexes of samarium and terbium with axial ligands: synthesis, structure and optoelectronic properties

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Abstract: The monophthalocyanine complexes of samarium and terbium containing axial 2-mercaptobenzothiazole (PcSm(MBT) (**1**)), 2-(2-benzoxazol-2-yl) phenolate (PcTb(OON) (**2**)) or 2-(2-benzothiazol-2-yl)phenolate (PcTb(SON) (**3**)) ligands were synthesized and identified by elemental, LDI-TOF and X-ray (for **1**) analysis. Photoluminescence (PL) and electroluminescence (EL) spectra of the compounds contained only emission bands of phthalocyanine and axial ligands but did not contain the bands of f-f transitions. It was found that among the complexes **1**, **2**, **3** the latter had highest photoconductivity (~10^{-7} S/cm) and photovoltaic properties. An organic photovoltaic device (OPV) of configuration of ITO/**3**/C_{60}/Alq_3/Al revealed open-circuit voltage (V_{OC}) of 0.24 V and short current density (I_{SC}) of 0.3 μA/cm^2 under illumination by a xenon lamp at 17 mW/cm^2.

Keywords: phthalocyanine; samarium; terbium; luminescence; photovoltaic; OLED; rare earths

Phthalocyanine metal complexes have been studied intensively for many years[1]. Great interest in these compounds is stipulated by unusual chemical and physical properties which determine their use as dyes[2], semiconductors[3–9], hole-injecting layers in OLED devices[10,11], materials for photovoltaic cells[12–14] and photosensitizers in photodynamic therapy of cancer[15]. Phthalocyanine complexes of rare earth metals represent a significant and very important part of these materials[16]. The lanthanide monophthalocyanine complexes with axial ligands are especially promising because the properties of the compounds in this case can be varied not only by changing the nature of the phthalocyanine moiety and the metal center, but also by modifying the axial group[17–19].

Recently we have found that complexes of samarium and terbium with a 2-mercaptobenzothiazole[20–22], 2-(2-benzoxazolyl)phenolate and 2-(2-benzothiazolyl) phenolate[23,24] ligands are effective electroluminophores. In this work we combined both types of the sensitizing ligands (phthalocyanine and aromatic chelate groups) in one molecule and studied their luminescence and photovoltaic properties.

1 Experimental

1.1 General procedures

Syntheses were carried out under standard Schlenk techniques. Sodium benzophenone ketyl solution was used to prepare anhydrous, oxygen-free THF and DME solvents distilled before further manipulations. 2-Mercaptobenzothiazole, 2-(2-benzoxazol-2-yl)phenole, 2-(2- benzothiazol-2-yl)phenole and phthalocyanine were purchased from Sigma-Aldrich and used without additional purification. The lanthanide complexes $Ln[N(SiMe_3)_2]_3$ were obtained according to published procedure[25]. IR spectra were obtained on a Perkin-Elmer 577 spectrometer and recorded from 4000 to 450 cm^{-1} as a Nujol mull on KBr plates. Absorption and PL spectra were recorded using a Perkin-Elmer Lambda 25 and Perkin-Elmer LS 55 spectrometers respectively.

The X-ray diffraction data for compound **1** were collected on a SMART APEX diffractometer (graphite-monochromated, Mo Kα radiation, θ-scan technique, λ=0.071073 nm). The intensity data were integrated by the SAINT program[26]. SADABS[27] was used to perform area-detector scaling and absorption corrections. The structure was solved by direct methods and refined on F^2 using all reflections with the SHELXTL package[28]. All non-hydrogen atoms were refined anisotropically. H atoms were located in calculated positions and

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refined in "the riding-model". The crystal data and details of the structure determinations for **1** are summarized in Table 1. CCDC-978751 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

The mass spectra were recorded on a Bruker Microflex LT mass spectrometer. A small quality of sample (less than 1 mg) was placed on a ground steel target plate and was ground by stainless steel spatula. The excess of powder was removed by cotton pellet. The samples were excited at a wavelength of 337 nm at a maximum pulsed laser beam intensity of 150 μJ per pulse at 60 Hz. The LDI- TOF-MS spectra were taken as described in detail elsewhere by summarizing 300–400 single mass spectra from three-four different points of each sample.

1.2 Synthesis

1.2.1 Phthalocyanine(2-mercaptobenzothiazole)-samarium [SmPc(MBT)(DME)(THF)] (**1**).

A solution of $Sm[N(SiMe_3)_2]_3$ (0.144 g, 0.228 mmol) in THF (15 mL) was added to a mixture of 2-mercaptobenzothiazole (0.038 g, 0.227 mmol) and phthalocyanine (0.117 g, 0.227 mmol).

The reaction mixture was stirred for 48 h at 60 ºC. The greenish blue solution obtained was filtered and the solvent was evaporated under vacuum to give a solid residue which was recrystallized from THF/DME mixture to give **1** as bluish-violet crystals (0.135 g, 60%). Anal. calcd. for $SmS_2C_{47}H_{38}N_9O_3$ (991.35): C, 56.94; H, 3.86; S, 6.47; Sm, 15.17. Found: C, 56.62; H, 4.05; S, 6.25; Sm, 15.47%. UV-vis absorption spectrum in THF, λ_{max} nm (lg ε): 330 (1.31); 606 (0.23); 642 (0.22); 671 (1.23). IR (ν, cm^{-1}): 1653(sh), 1599(m), 1583(m), 1560(m), 1524(m), 1497(sh), 1483(s), 1429(s), 1329(sh), 1321(s), 1284(m), 1260(sh), 1247(m), 1160(m), 1129(m), 1114(m), 1080(s), 1060(s), 1034(s), 1025(s), 1014(s), 932(w), 884(m), 849(m), 816(m), 777(sh), 751(s), 732(s), 670(m), 629(m), 605(m), 570(m), 525(w), 499(m), 425(m).

1.2.2 Terbium phthalocyanine(2-(2-benzoxazol-2-yl) phenolate [TbPc(OON)(THF)] (**2**)

A solution of $Tb[N(SiMe_3)_2]_3$ (0.13 g, 0.203 mmol) in THF (15 mL) was added to a mixture of 2-(2-hydroxyphenyl)benzoxazole (0.043 g, 0.204 mmol) and phthalocyanine (0.105 g, 0.204 mmol). The reaction mixture was stirred for 48 h at 60 ºC to give a solid residue. The residue was filtered, washed with THF (15 mL×2) and dried in vacuo. Product **2** was obtained as a bluish-green noncrystalline powder (0.187 g, 96%). Anal. calcd. for $C_{49}H_{32}N_9O_3Tb$ (953.76): C, 61.64; H, 3.48; N, 13.20; Tb, 16.65. Found: C, 61.81; H, 3.30; N, 13.64; Tb, 16.86%. UV-vis absorption spectrum in THF, λ_{max} nm (lg ε): 336(2.25); 620(1.16); 676(1.84). IR (ν, cm^{-1}): 1747(m), 1608(sh), 1598(m), 1526(m), 1332(m), 1308(m), 1283(m), 1260(w), 1234(w), 1156(m), 1115(m), 1077(m), 1060(m), 1003(w), 893(w), 884(w), 847(w), 820(w), 801(w), 775(w), 630(w).

1.2.3 Terbium phthalocyanine(2-(2-benzothiazol-2-yl) phenolate [TbPc(SON)(THF)] (**3**)

Complex **3** was obtained in a similar manner as complex **2** from $Tb[N(SiMe_3)_2]_3$ (0.122 g, 0.191 mmol), 2-(2-hydroxyphenyl)benzothiazole (0.044 g, 0.194 mmol) and phthalocyanine (0.098 g, 0.191 mmol). The yield of **3** was 0.078 g (82%). Anal. calcd. for $C_{49}H_{32}N_9O_2STb$ (969.83): C, 60.68; H, 3.33; N, 13.00; Tb, 16.39. Found: C, 60.56; H, 3.13; N, 12.76; Tb, 16.94%. UV-vis absorption spectrum in THF, λ_{max} nm (lgε): 332(0.47); 602(0.22); 638(0.21), 665(0.99). IR (ν, cm^{-1}): 1606(m), 1589(m), 1556(m), 1483(s), 1406(m), 1332(s), 1317(m), 1284(m), 1267(m), 1251(m), 1234(m), 1215(m), 1204(m), 1161(m), 1116(s), 1076(s), 1061(s), 1016(m), 1003(m), 976(m), 954(m), 929(m), 884(m), 870(m), 844(m), 823(m), 795(w), 777(m), 745(s), 730(s), 630(m), 586(w), 565(w), 551(w), 537(w), 512(w), 496(m).

Table 1 X-Ray data collection and refinement parameters for complex 1

Empirical formula	$C_{47}H_{38}N_9O_3S_2Sm$
Formula weight	991.33
Temperature/K	100(2)
Wavelength/nm	0.071073
Crystal system, space group	Monoclinic, $P2_1/c$
a/nm	1.53370(5)
b/nm	1.34483(5)
c/nm	1.97914(7)
α/(º)	90
β/(º)	93.115(1)
γ/(º)	90
Volume/nm^3	4.0761(2)
Z, calculated density/(kg/m^3)	4, 1.615×10^3
Absorption coefficient/mm^{-1}	1.600
F(000)	2004
Crystal size/mm	0.23×0.22×0.20
θ Range for data collection/(°)	1.33–26.00
Limiting indices	$-18\le h\le 18$, $-16\le k\le 16$, $-24\le l\le 24$
Reflections collected/unique	33926 / 7953
Rint	0.0276
Data/restraints/parameters	7953 / 19 / 565
Goodness-of-fit on F^2	1.062
Final R indices [$I>2\sigma(I)$]	R_1=0.0305 wR_2=0.0710
R indices (all data)	R_1=0.0417 wR_2=0.0749
Largest diff. peak and hole/($e\times nm^{-3}$)	1.412×10^{-6} / -1.005×10^{-6}

1.3 OLED devices fabrication

The devices ITO/**1** (10 nm)/TPD (40 nm)/BATH (50 nm)/Yb (150 nm) and ITO/**1** (10 nm)/TPD (20 nm)/$[Er(NpSON)_3]_2$ (50 nm)/Yb (150 nm), consisting of triphenyldiamine derivative (TPD) as a hole transport layer, 4,7-diphenyl-1,10-phenanthroline (BATH) as a