Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Sandwich-type phthalocyaninato metal sextuple-decker complex. Synthesis and NLO properties

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Caption of Content

Experimental Section

General Remarks. All the reagents and solvents were used as received. The compound $Sm[Pc^*]_2$ was prepared according to the published procedure.[1] ^1H NMR and ^1H-^1H COSY spectra were recorded on a Bruker DPX 400 spectrometer in $CDCl_3$. Spectra were referenced internally using the residual solvent resonance (δ = 7.26) relative to $SiMe_4$. Electronic absorption spectrum was recorded on a Hitachi U-4100 spectrophotometer. MALDI-TOF mass spectrum was taken on a Bruker BIFLEX III ultrahigh resolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with α-cyano-4-hydroxycinnamic acid as the matrix. Elemental analysis was performed on an Elementar Vavio El III elemental analyzer. Electrochemical measurement was carried out with a BAS CV-50W voltammetric analyzer. The cell comprised inlets for a glassy carbon disk working electrode with a diameter of 2.0 mm and a silver wire counter electrode. The reference electrode was Ag/Ag^+ (a solution of 0.01 M $AgNO_3$ and 0.1 M $[Bu_4N][ClO_4]$ in acetonitrile), 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 using ferrocenium/ferrocene (Fe^+/Fe) couple [$E_{1/2}$ (Fe^+/Fe) = 0.50 V vs SCE] as an internal reference. Typically, a 0.1 M solution of $[NBu_4][ClO_4]$ in CH_2Cl_2 containing 0.5 mM of the sample was purged with nitrogen for 10 min, and then the voltammograms were recorded at room temperature with scan rate of 40 mV s^{-1} for cyclic voltammetry (CV).

Synthesis of [(Pc*)Sm(Pc*)Cd(Pc*)Cd(Pc*)Cd(Pc*)Sm(Pc*)] (1)*: A mixture of $Cd(OAc)_2.2H_2O$ (10.6 mg, 0.04 mmol), neutral bis[2,3,9,10,16,17,23,24-octa(butyloxy)phthalocyaninato] samarium double-decker compound $Sm(Pc^*)_2$ (0.01 mmol), and metal free 2,3,9,10,16,17,23,24-octa(butyloxy)phthalocyanine (20.8 mg, 0.02 mmol) in 1,2-4-trichlorobenzene (TCB) (3 mL) was heated to reflux under nitrogen for 4.5 h. After being cooled to room temperature, the volatiles were removed under reduced pressure. The residue was chromatographed on a silica gel column using $CHCl_3$ as the eluent to give a green band, which contained the unreacted $Sm(Pc^*)_2$. Further elution with $CHCl_3/CH_3OH$ (95:5) gave a blue band containing the sextuple-decker complex [(Pc*)Sm(Pc*)Cd(Pc*)Cd(Pc*)Cd(Pc*)Sm(Pc*)] (**1**) as well as quadruple- and quintuple-decker complexes [(Pc*)Sm(Pc*)Cd(Pc*)Cd(Pc*)Sm(Pc*)] and [(Pc*)Sm(Pc*)Cd(Pc*)Sm(Pc*)] as side products. Further repeated biobead column chromatography followed by recrystallization from chloroform and methanol gave the pure target homoleptic hexakis[2,3,9,10,16,17,23,24-octa(butyloxy)phthalocyaninato] samarium-cadmium sextuple-decker complex **1** in the yield of 8.3 %. MS (MALDI-TOF) for **1**: an isotopic cluster peaking at *m/z* 7174.48 (Calcd. for M^+ 7174.17). Anal. Calcd. for $C_{384}H_{480}Cd_3N_{48}O_{48}Sm_2(3CHCl_3)$: C 61.71, H 6.46, N 8.92; Found: C 61.51, H 6.70, N 8.75. The electronic absorption data for **1** in $CHCl_3$ λ_{max} (log ε): 346 (5.52) and 640 (5.33) nm.

References

1 (a) J. Jiang, R. C. W. Liu, T. C. W. Mak, T. W. D. Chan and D. K. P. Ng, *Polyhedron,* 1997, **16**, 515; (b) W. Liu, J. Jiang, D. Du, D. P. Arnold, *Aust. J. Chem.,* 2000, **53**, 131; (c) J. Jiang, J. Xie, D. K. P. Ng, Y. Yan *Mol. Cryst. Liq. Cryst.,* 1999, **337**, 385.

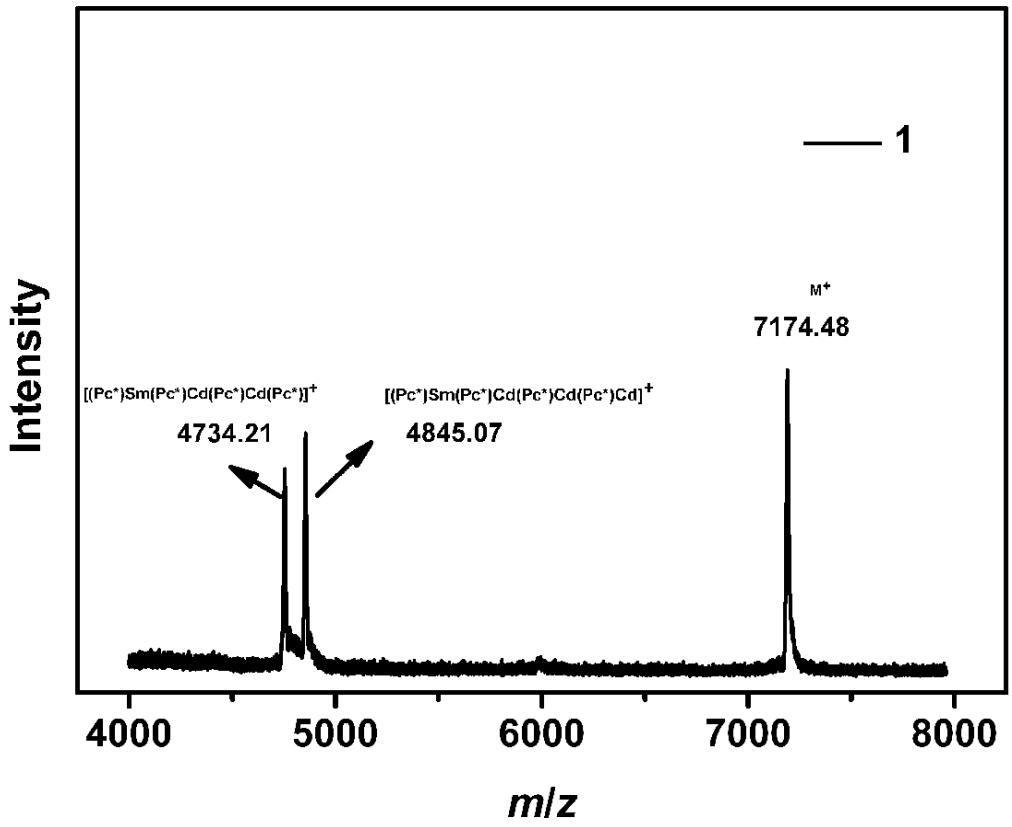

Figure S1. MALDI-TOF mass spectrum of (Pc*)Sm(Pc*)Cd(Pc*)Cd(Pc*)Cd(Pc*)Sm(Pc*) (**1**).

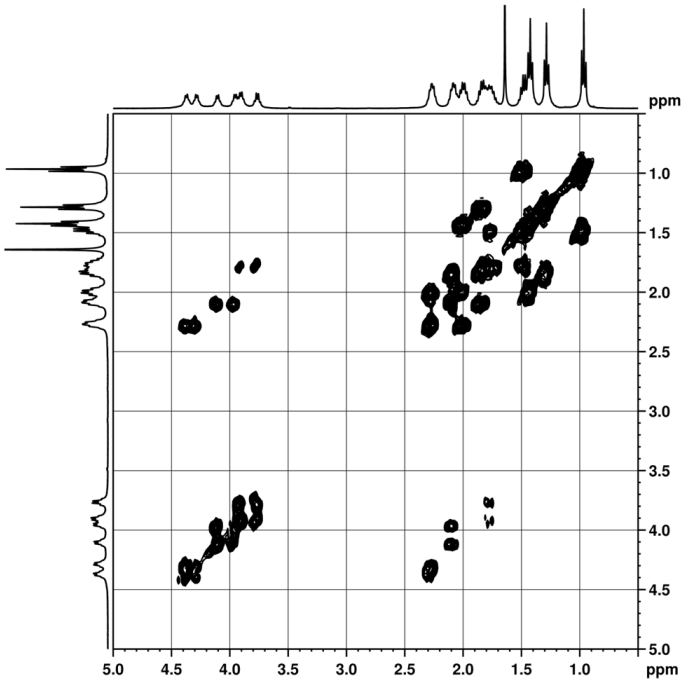

Figure S2. ^{1}H-^{1}H COSY spectrum of sextuple-decker compound **1** in $CDCl_3$.

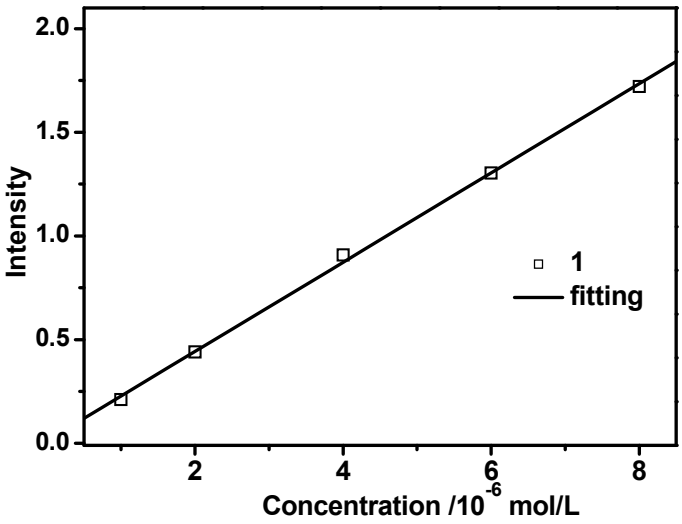

Figure S3. Beer-Lambert plot for **1** in the toluene.

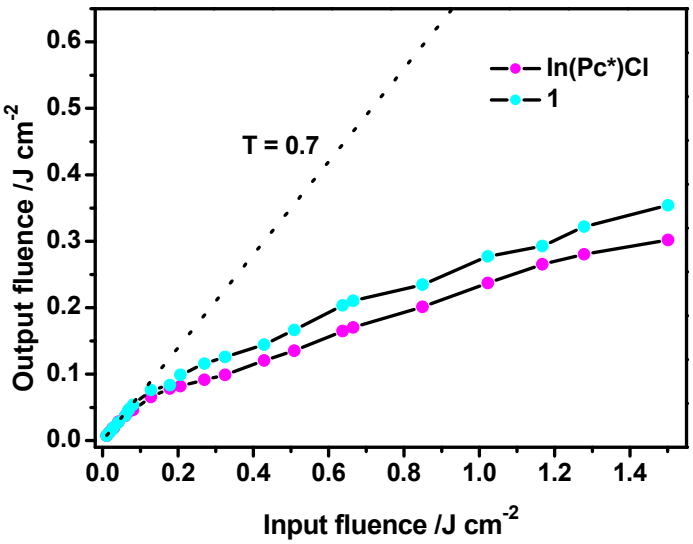

Figure S4. Optical limiting properties of **1** and In(Pc*)Cl in toluene under 532 nm nanosecond laser with the linear transmittance of 0.7.

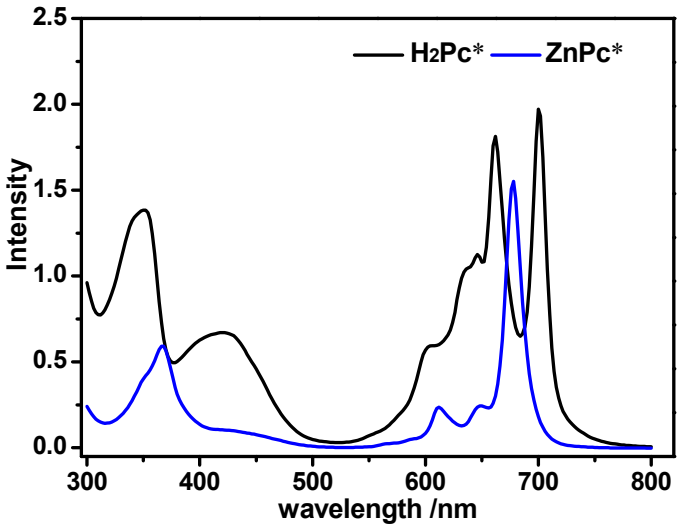

Figure S5. Electronic absorption spectra of H_2Pc^* and ZnPc* in toluene with the concentration of 5.0×10^{-6} mol/L.

Table S1. ^{1}H NMR data (δ) and assignments of the sextuple-decker **1** in $CDCl_3$.

Complex	location	$\mathbf{H}^{\alpha}$	-O$\mathbf{CH_2}$-	-OCH$_2\mathbf{CH_2}$-	-O(CH$_2$)$_2\mathbf{CH_2}$-	-O(CH$_2$)$_3\mathbf{CH_3}$
1	first outer	6.32 (s, 16H)	3.93 (m, 16H) 3.77 (m, 16H)	1.86 (m, 32H)	1.49 (m, 32H)	0.98 (t, 48H)
	second outer	6.70 (s, 16H)	4.11 (m, 16H) 3.96 (m, 16H)	2.10 (s, 32H)	1.86 (m, 32H)	1.30 (s, 48H)
	central outer	7.11 (s, 16H)	4.38 (m, 16H) 4.29 (m, 16H)	2.28 (s, 32H)	2.02 (m, 32H)	1.44 (s, 48H)

Table S2. The effective imaginary third order molecular hyperpolarizability (Im$\{\chi^{(3)}\}$) data for complex **1**.

concentration	1×10^{-5} mol/L	2×10^{-5} mol/L	1.2×10^{-4} mol/L
(Im$\{\chi^{(3)}\}$) /esu	5.98×10^{-12}	1.04×10^{-11}	1.91×10^{-11}