Electronic Supplementary Information

Sextuple-Decker Heteroleptic Phthalocyanine Heterometallic Samarium−Cadmium Complex with Crystal Structure and Nonlinear Optical Property in Solution and Gel Glass

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S1. Experimental Section

General remarks. All the reagents and solvents were used as received. The compound sextuple-decker complex {(Pc)Sm(Pc)Cd(Pc*)Cd(Pc*)Cd(Pc)Sm(Pc)} (**1**) was prepared according to the published procedure.[1]

Synthesis of sextuple-decker complex 1. A mixture of $Cd(OAc)_2 \cdot 2H_2O$ (5.3 mg, 0.02 mmol), H_2Pc^* (12.0 mg, 0.01 mmol) and $SmPc_2$ (11.8 mg, 0.01 mmol) in TCB (2.9 g, 16 mmol) was heated to reflux under nitrogen for 4.0 hours. After cooling, the mixture was evaporated under reduced pressure, and the residue was chromatographed on a silica gel column and gel permeation chromatography using chloroform as eluent. Then followed by recrystallization from dichloromethane and methanol afforded dark-blue microcrystals of target products of **1** (3.8 mg, 0.80 μmol, for products: 15.1%). For **1**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.54 (m, 16H), 7.24 – 7.18 (m, 16H), 7.16 (dd, J = 5.1, 2.9 Hz, 16H), 7.11 (s, 16H), 7.05 (dd, J = 4.9, 2.9 Hz, 16H), 4.52 (dq, J = 23.7, 6.7 Hz, 32H), 2.42 (tt, J = 12.8, 6.5 Hz, 32H), 2.04 (p, J = 7.5 Hz, 32H), 1.88 (h, J = 7.2 Hz, 32H), 1.38 (t, J = 7.3 Hz, 48H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.97, 150.33, 134.34, 132.89, 127.86, 127.60, 122.78, 120.91, 106.32, 69.54, 29.83, 29.08, 23.19, 14.70. UV-vis (CH_2Cl_2): λ_{max} (log ε) 293 (5.27), 336 (5.43), 623 (5.33), 670 nm (4.85). MS (MALDI-TOF) *m*/*z*: $[M]^+$ calcd for $C_{272}H_{256}Cd_3N_{48}O_{16}Sm_2$, 5091.9; found: 5091.2. Elemental analysis of **1** calcd. (%) for $C_{272}H_{256}Cd_3N_{48}O_{16}Sm_2$: C 64.17, H 5.07, N 13.21; found: C 64.50, H 4.69, N 13.28.

Physical characterizations. ^{1}H NMR, ^{13} C NMR and ^{1}H – ^{1}H COSY spectra were recorded on a Bruker DPX 400 spectrometer in $CDCl_3$. Spectrum was referenced internally using the residual solvent resonances (δ = 7.26 for ^{1}H NMR and 77.16 for ^{13} C NMR). The electronic absorption spectra were collected using a Perkin-Elmer Lambda 750 UV-vis spectrophotometer. IR spectra were recorded using a Bruker Tensor 37 spectrometer with 2 cm^{-1} resolution. MALDI-TOF mass spectrum was taken on a Bruker BIFLEX III ultra-high-resolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with alpha-cyano-4-hydroxycinnamic acid as matrix. The third order nonlinear optical property was studied using the Z-scan technique with a Nd-YAG laser as the light source (a pulse width of 6 ns and wavelength of 532 nm). MCD spectrum was determined using a JASCO J-815 CD spectropolarimeter. TGA was performed on a ZRT-A thermogravimetric analyzer over a temperature range of 35–800 °C under a nitrogen atmosphere with a heating rate of 10 °C min^{-1}. Powder X-ray diffraction (PXRD) data was collected with an X-ray diffractometer (PANalytical, Empyrean) operated at 45 kV and 40 mA with Cu Kα radiation. Elemental analysis was performed using an Elementar Vario El III instrument. Electrochemical measurement was carried out with a CHI760E voltammetric analyzer. The reference electrode was Ag^{+}/Ag (a solution of 0.01 M $AgNO_3$ and 0.1 M TBAP in acetonitrile), which was connected to the solution by a Luggin capillary, whose tip was placed close to the working electrode. Typically, a 0.1 M solution of $[NBu_4][ClO_4]$ in $CHCl_3$ purged with nitrogen for 10 min, and then the voltammogram was recorded at ambient temperature.

Single crystal X-ray diffraction analysis. Crystal data for **1** was determined by X-ray diffraction analysis at 150 K using a diffractometer of SuperNova, Dual, Cu at home/near, AtlasS2 with Mo Kα radiation λ = 0.7107 Å, and details of the structure refinement are given in Table S1. The structure was solved by direct methods with *SHELXS-2018* and refined on F^2 by full-matrix least-squares applying *SHELXTL-2018* within WINGX.[2-4] Anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms. Hydrogen atoms were added geometrically and refined using a riding model. The SQUEEZE routine in PLATON was applied to remove the highly disordered solvents.[5] CCDC 2009851 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.

Theoretical calculations. The geometry of $\mathbf{1}^{\#}$ was fully optimized and the C_4 point group was used during optimization. No imaginary frequency was found, indicating the optimized structure of $\mathbf{1}^{\#}$ with C_4 symmetry being real minimum. Orbital energies were calculated based on the optimized geometry of $\mathbf{1}^{\#}$ without further optimization. All calculations were performed with the hybrid density functional B3LYP (Becke-Lee-Young-Parr composite of exchange-correlation functional) method,[6] LANL2DZ effective core potential[7] for Y and Cd, and 6-31G(d) basis set for other elements using

Gaussian 09 software package.[8]

Preparation of Gel Glass. The **1**/MTES gel glass were prepared with a modified method of a previous report[9], by using hydrolysis and polycondensation of MTES (170 mL) in acetic acid medium (H_2O/ethanol, 54mL/600mL, pH = 2) for one day. The mixture was evaporated half of the solvent and then stirred at room temperature for 7 days, and saved in sealed. Then a solution (0.3, 0.6, 0.9, 1.2, and 1.5 mL) of **1** in $CHCl_3$ (0.5 mg/mL) was added into the mixture MTES gel (12 mL, pH = 5.5) at a certain mass concentration and fully stirred to produce gel glass, **G1-G5** (1, 2, 3, 4, and 5 wt‰ with mass ratios of **1**/MTES), respectively. Finally, the mixed sols were dried for five days at room temperature and 2 days at 50℃ to obtain the **1**/MTES gel glass with uniform thicknesses.

S2. Characterizations

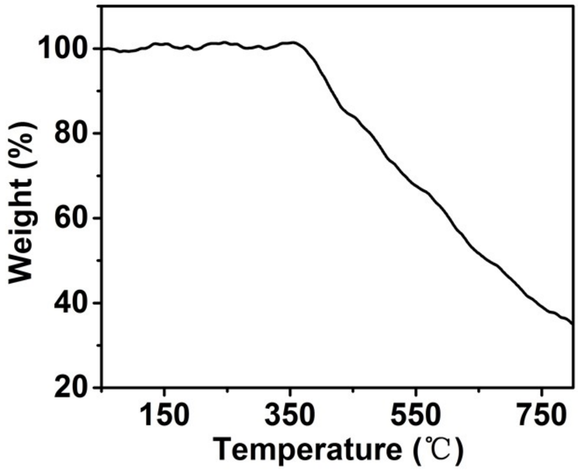

Fig. S1. TGA curve of **1** in the range of 25-800°C under N_2 atmosphere.

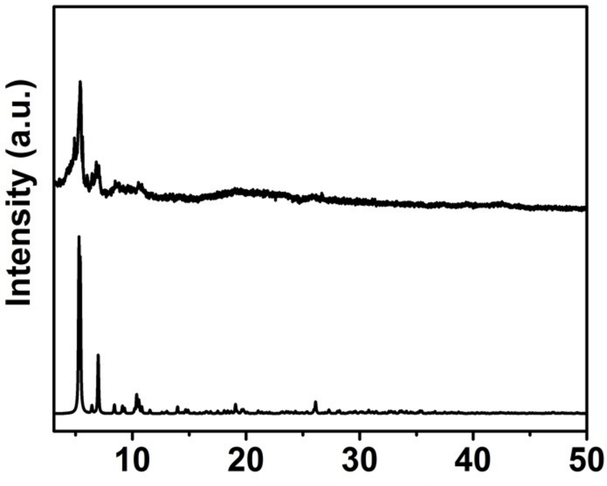

Fig. S2. Powder X-ray diffraction profiles for as-prepared **1** (top) in comparison with a simulated powder pattern (bottom) based on the **1** single-crystal structure without considering the solvent molecules.

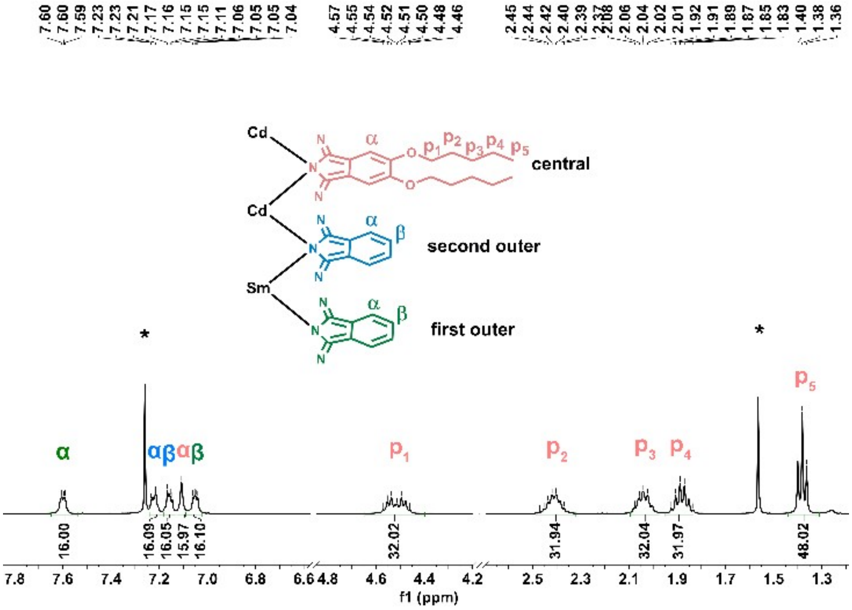

Fig. S3. ^{1}H NMR spectrum of **1** in $CDCl_3$ (asterisks denote $CDCl_3$ solvent impurity).

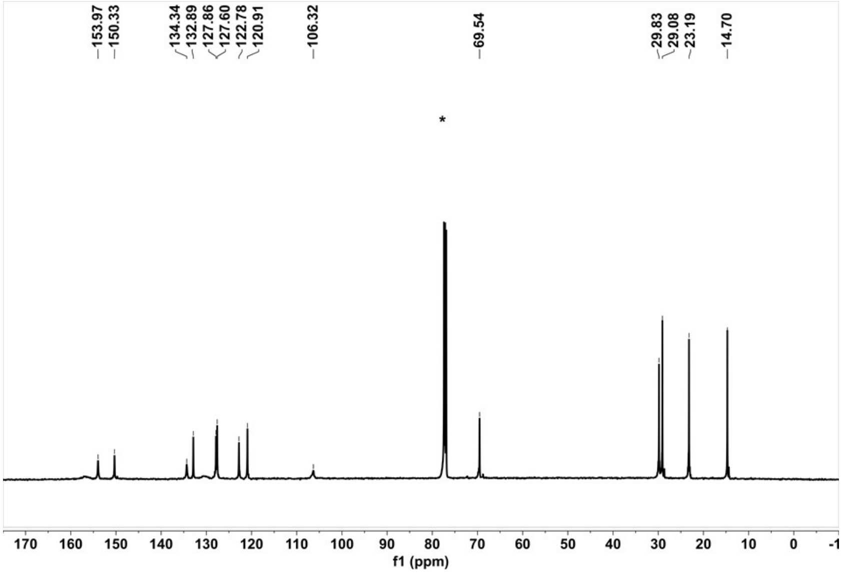

Fig. S4. ^{13}C NMR spectrum of **1** (* denotes $CDCl_3$ solvent impurity).

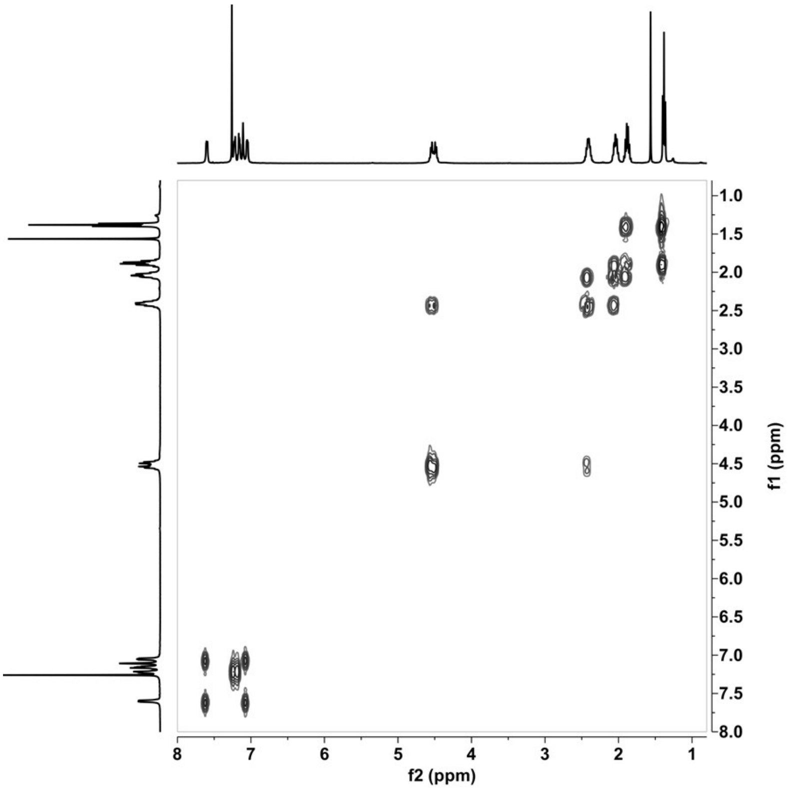

Fig. S5. ^{1}H-^{1}H COSY spectrum of **1** in $CDCl_3$.

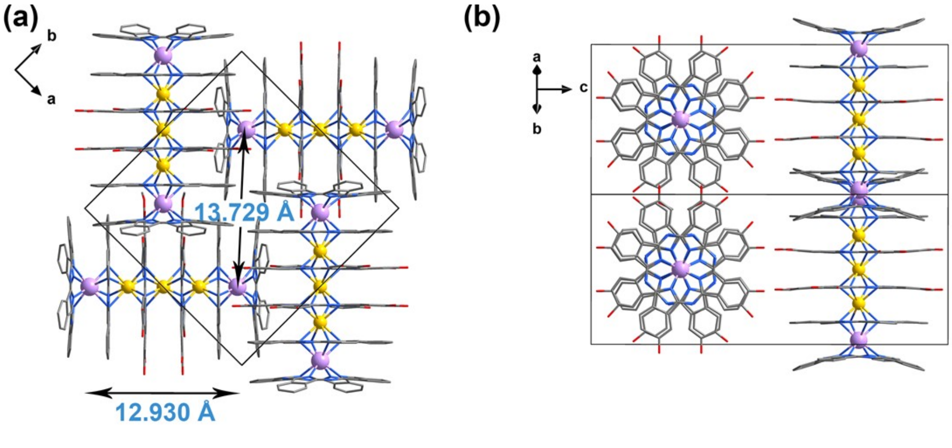

Fig. S6. Packing plots of **1** in the different views.

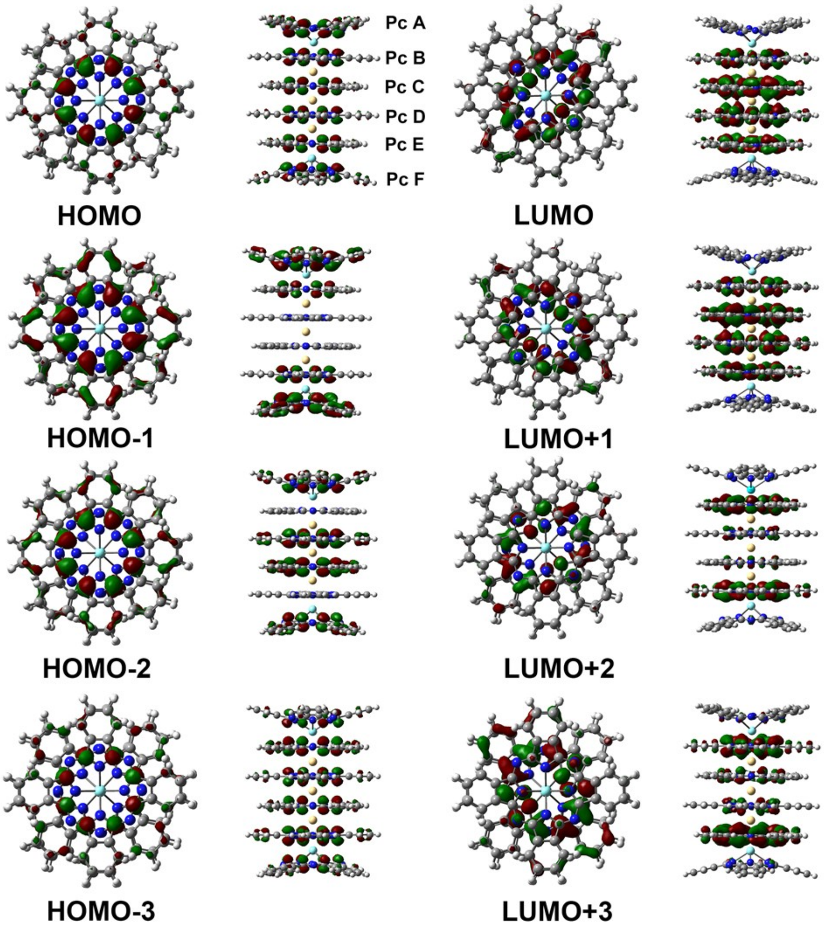

Fig. S7. Maps of the frontier MOs of **1**$^{\#}$.

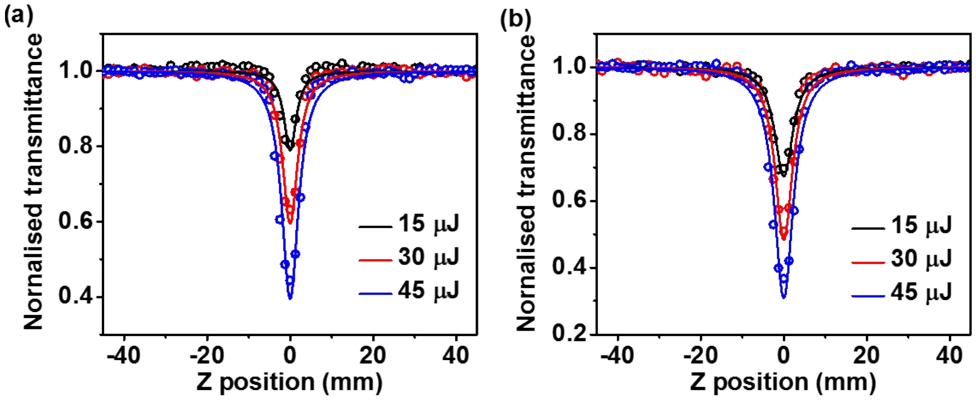

Fig. S8. NLO absorptive property of **1** in $CHCl_3$ solution with the concentrations of 6.0×10^{-5} mol L^{-1} (a) and 1.0×10^{-4} mol L^{-1} (b) at different incident intensity.

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

location	H^{α}	H^{β}	$-O\mathbf{CH_2}-$	$-OCH_2\mathbf{CH_2}-$	$-OCH_2CH_2\mathbf{CH_2}-$	$-OCH_2CH_2CH_2\mathbf{CH_2}-$	$-OCH_2CH_2CH_2CH_2\mathbf{CH_3}$
first outer	7.65 (m, 16H)	7.05 (dd, 16H)					
second outer	7.24 (m, 16H)	7.16 (dd, 16H)					
central	7.11 (s, 16H)		4.52 (dq, 16H)	2.42 (tt, 32H)	2.04 (p, 32H)	1.88 (h, 32H)	1.38 (t, 48H)

Table S2. Crystal data and structure refinements for **1**.

Compound	**1**
formula	$C_{272}H_{256}Cd_3N_{48}O_{16}Sm_2$
fw	5091.13
crystal system	Tetragonal
space group	*P*-4*n*2
a /Å	19.3851(5)
b /Å	19.3851(5)
c /Å	32.6490(15)
α /°	90
β /°	90
γ /°	90
V /Å^3	12268.9(8)
Z	2
θ range (deg)	3.497-66.590
Density (g/cm^3)	1.378
μ(mm^{-1})	6.167
F(000)	5240
R_1 (I>2θ)[a]	0.0707
R_{w2} for all[b]	0.2222
GOF on F^2	0.939
CCDC No.	2009851

[a] $R_1 = \Sigma|F_o\text{-}|F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2\text{-}F_c^2)^2/\Sigma w(F_o^2)^2]^1$

Table S3. The distribution over metals and different Pc rings for the frontier molecular orbitals of **1'**.

	HOMO-3	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2	LUMO+3
Pc A	14.464%	23.745%	32.995%	20.241%	1.05%	1.05%	3.369%	3.369%
Y	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
Pc B	19.377%	0.335%	13.935%	15.849%	17.469%	17.469%	36.535%	36.535%
Cd	0.00%	0.00%	0.00%	0.00%	0.062%	0.062%	0.097%	0.097%
Pc C	16.078%	25.963%	1.816%	15.084%	31.061%	31.061%	9.665%	9.665%
Cd	0.00%	0.00%	0.00%	0.00%	0.052%	0.052%	0.252%	0.252%
Pc D	15.923%	26.127%	1.979%	14.702%	31.162%	31.162%	9.407%	9.407%
Cd	0.00%	0.00%	0.00%	0.062%	0.062%	0.062%	0.099%	0.099%
Pc E	19.837%	0.389%	14.537%	14.980%	17.728%	17.728%	36.622%	36.622%
Y	0.00%	0.00%	0.00%	0.00%%	0.037%	0.037%	0.101%	0.101%
Pc F	14.320%	23.440%	34.736%	19.144%	1.052%	1.052%	3.323%	3.323%

Table S4. The effective imaginary third order molecular hyperpolarizability (Im{$\chi^{(3)}$}) data for the series of sandwich-type complex **1**.

	Im{$\chi^{(3)}$}		
Concentration	15 μJ	30 μJ	45 μJ
2.0×10^{-5} mol L^{-1}	7.14×10^{-11} esu	5.76×10^{-10} esu	2.23×10^{-10} esu
6.0×10^{-5} mol L^{-1}	1.02×10^{-10} esu	4.78×10^{-10} esu	1.20×10^{-9} esu
1.0×10^{-4} mol L^{-1}	2.37×10^{-10} esu	7.32×10^{-10} esu	1.55×10^{-9} esu

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