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Electrochromic properties of novel octa-pinene substituted double-decker Ln(III) (Ln = Eu, Er, Lu) phthalocyanines with distinctive near-IR absorption

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Octa-pinene substituted double-decker lanthanide(III) phthalocyanines **LnPc*₂** (Ln = Eu, Er, Lu) were prepared and their spectral, electrochemical, spectroelectrochemical and electrochromic properties were studied. The introduction of the bulky and rigid pinene groups into phthalocyanine provides several advantages for the resulting double-decker lanthanide(III) phthalocyanines complex. First of all, the intermolecular interaction in the new **LnPc*₂** complex was weakened, leading to excellent solubility. Secondly, intramolecular distances between the macrocycles in **LnPc*₂** molecules was also increased, resulting in significant red shift for the ring-to-ring inter valence charge transfer bands. Particularly, the inter valence bands of **EuPc*₂**, **ErPc*₂** and **LuPc*₂** were observed at 1944, 1693 and 1620 nm, respectively, which appear to be the most red-shifted absorption in comparison with the literature values of mononuclear double-decker Eu(III), Er(III) and Lu(III) phthalocyanines. Thirdly, given the red-shifted near-IR (NIR) absorption and the various colorful oxidation states, the solution of **LnPc*₂** exhibit electrochromic behavior both in the UV-Vis and near-IR region. Notably, spectra change of **EuPc*₂** covers almost the whole range of NIR region. Finally, the pinene groups also enhance the film-forming ability. Therefore, we were able to fabricate solid state electrochromic devices through solution processable method. The as fabricated devices show reversible electrochromic behavior with high color efficiency and good stability.

Introduction

Double-decker lanthanide(III) phthalocyanines are currently the object of multiple investigations as a consequence of their exceptional physical and chemical properties.^[1] Of particular interest is their reversible redox properties. Double-decker lanthanide(III) phthalocyanines can be reversibly oxidized by up to four electrons or reversibly reduced by up to two electrons, leading to various oxidation states with different colors.^[2] Moreover, due to the presence of π -radicals, bis(phthalocyaninato) rare earth complex show an intramolecular charge-transfer in the 1200–1500 nm range.^[3] Oxidation of the π -radical causes changes of spectrum in near-IR (NIR) region. Such features are very useful for electrochromic devices both in UV-Vis (380–780 nm) and NIR region (780–2500 nm), with wide applications like smart windows, displays, computer data storage, active optical filters, and thermal control (heat gain or loss) in buildings and spacecrafts.^[4]

As a result of the strong intermolecular interaction between the macrocycles, peripherally unsubstituted double-decker lanthanide(III) phthalocyanines are practically insoluble in common organic solvents, which limits their applications. Therefore, various substituents, such as alkyl, alkoxy or phenoxy groups, were introduced on the peripheral and/or

nonperipheral sites of the phthalocyanine ring in order to improve their solubility.^[5] As part of our continuing effort in developing pinene-functionalized coordination complex,^[6] herein we introduced pinene groups into double-decker lanthanide(III) phthalocyanine complex.

Pinene group is a bulky and rigid alkyl ring with remarkable steric hindrance. According to previous study, the intramolecular charge-transfer double-decker lanthanide(III) phthalocyanine in the 1416 ~ 2250 nm range is very sensitive to the intramolecular π - π distances. Consequently, this absorption bands are monotonically blue-shifted along with the decrease of the ionic radius from La(III) to Tm(III).^[1b] When pinene groups are introduced, the rigid rings will decrease the interaction between the macrocycles in **LnPc*₂** molecules, which result in lower energy transfer from second-highest occupied orbital to the semi-occupied orbital. Moreover, pinene is a strong electron-donating group. The introduction of pinene will change the frontier orbitals and therefore spectral properties. Therefore, good solubility as well as nontrivial spectral and electrochemical properties are expected for octa-pinene substituted double-decker lanthanide(III) phthalocyanine complex.

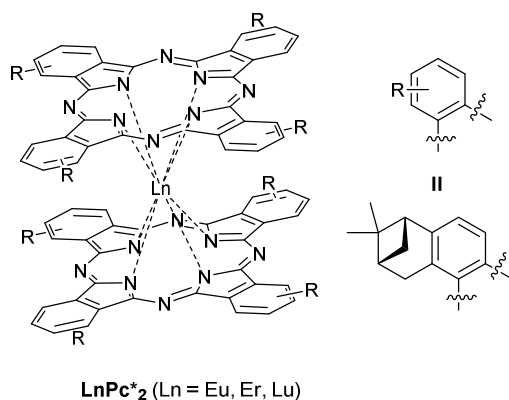


Figure 1. Structure of octa-pinene substituted double-decker phthalocyanines (only C_{4v} shown).

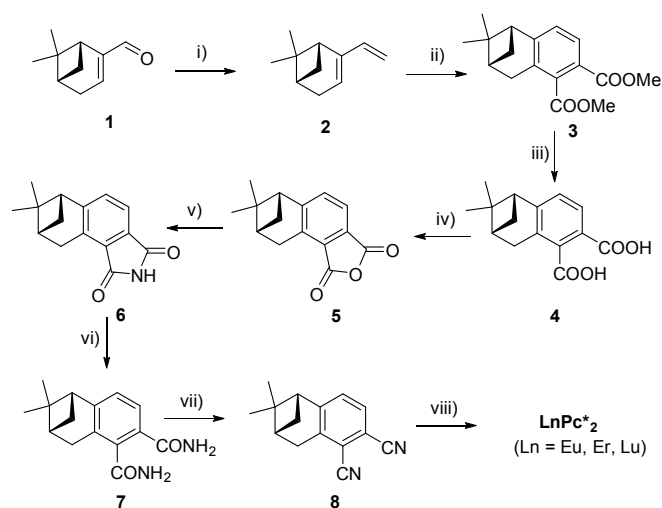
In this work, we report the synthesis, UV-Vis-NIR and Raman spectra, voltametric, *in-situ* spectroelectrochemical, and electrochromic properties of double-decker lanthanide(III) phthalocyanines bearing pinene substituents (Figure 1). The novel LnPc^*_2 ($\text{Ln} = \text{Eu}, \text{Er}, \text{Lu}$) complex have excellent solubility in common solvents. The inter valence (IV) bands of LnPc^*_2 show significant red shift compared with the published LnPc_2 derivatives. IV bands of EuPc^*_2 , ErPc^*_2 , LuPc^*_2 were observed at 1944, 1693 and 1620 nm, respectively. To the best of our knowledge, this absorption is the largest in the series of corresponding mononuclear Eu, Er and Lu double-decker phthalocyanine complex. Three quasi-reversible one-electron oxidations and five quasi-reversible one-electron reductions have been revealed for these neutral double-decker compounds. For ErPc^*_2 , an unprecedented sixth reduction reactions were also observed. The solution of LnPc^*_2 exhibit electrochromic behavior both in the UV-Vis and near-IR region. Notably, the spectra change of EuPc^*_2 covers almost the whole range of NIR region. Moreover, the new LnPc^*_2 complexes show good film-forming ability upon spin coating. Therefore, we were able to fabricate solid state electrochromic devices through solution processable method. The as fabricated devices show reversible electrochromic behavior with high color efficiency and good stability.

Experimental

General

All reagents and organic solvents (anhydrous grade) were purchased from commercial suppliers and used as received. Elemental analyses for C, H and N of the complex were performed on a perkin-Elmer 240C analyzer. Infrared spectra were recorded in KBr pellet on a vector 22 Bruker spectrophotometer in the range of 4000-400 cm^{-1} . UV/Vis/NIR spectra were measured on a UV-3600 spectrophotometer. Electronic circular dichroism spectra were performed on a Jasco J-810 spectropolarimeter. MS (MALDI-TOF) were recorded with a Bruker autoflex TOF mass spectrometer with 2,5-dihydroxybenzoic acid (DHB) as matrix. ^1H NMR spectra were performed on a Bruker DRX-500 spectrometer. Chemical shifts are given in ppm relative to SiMe_4 . Raman spectra were recorded on a few grains of solid samples with approximately 4 cm^{-1} resolution using a Hiroba LabRAM Aramis Confocal Raman Spectrometer, equipped with a Renishaw diode laser

excitation source emitting at a wavelength of 785 nm, and a cooled charge-coupled device (CCD) camera.



Scheme 1. Synthesis and molecular structure of complex 2 ~ 8 and LnPc^*_2 . i) MePPh_3Br , $t\text{-BuOK}$, THF; ii) DMAD, DDQ, toluene; iii) NaOH, HCl; iv) acetic anhydride; v) formamide; vi) $\text{NH}_3 \cdot \text{H}_2\text{O}$; vii) SOCl_2 , DMF; viii) $\text{Ln}(\text{acac})_3 \cdot \text{H}_2\text{O}$, DBU, *n*-hexanol.

Synthesis

(+)-nopadiene (2). To a suspension of methyltriphenylphosphonium bromide (3.87 g, 10.8 mmol) in anhydrous THF (25 ml) was added potassium tert-butoxide (1.21 g, 10.8 mmol). After stirring the mixture at room temperature for 0.5 h, (-)-myrtenal (1.50 ml, 9.86 mmol) was added. The reaction mixture was stirred at ambient temperature for 14 h, diluted with pentane (20 ml) and filtrated through a plug of celite eluting with pentane. The filtrate was eluted with pentane and concentrated in vacuum. The residue was purified by chromatography on silica gel and eluted with pentane to give the title compound as a colorless oil (1.39 g, yield: 95%). ^1H NMR (500 MHz, CDCl_3) δ (ppm): 6.37(1 H, m), 5.54-5.60 (1 H, m), 5.06 (1 H, m), 4.89 (1 H, d), 2.58 (1 H, m), 2.30-2.46 (3 H, m), 2.12-2.15 (1 H, m), 1.34 (3 H, s), 1.15 (1 H, d), 0.81 (3 H, s). ^{13}C NMR (500 MHz, CDCl_3) δ (ppm): 146.76, 137.81, 124.46, 109.54, 41.02, 40.30, 37.68, 31.85, 31.22, 26.34, 20.72. MS: m/z 147.50 [M]. Anal. Calcd. for $\text{C}_{11}\text{H}_{16}$: C, 89.12; H, 10.88. Found: C, 89.17; H, 10.80.

(1S,9S)-10,10-dimethyltricyclo[7.1.1.0^{2,7}]undeca-2,4,6-triene-5,6-dicarboxylate (3). Freshly distilled (+)-nopadiene (2) (725 mg, 5 mmol) was treated with dimethyl acetylenedicarboxylate (DMAD) (0.61 ml, 6 mmol). The mixture was stirred at 90 °C for 20 h and cooled to room temperature. 2, 3-dichloro-5, 6-dicyanobenzoquinone (DDQ) (1 g, 4.4 mmol) in 50 ml anhydrous toluene was added. The mixture was stirred for another 24 h. Toluene was removed under vacuum and the residue chromatographed on alumina with ether elution, to get a yellow oil (0.90 g, yield: 64%). ^1H NMR (500 MHz, CDCl_3) δ (ppm): 7.69 (1 H, d), 6.99 (1 H, d), 3.90 (3 H, s), 3.83 (3 H, s), 2.93 (2 H, m), 2.80 (1 H, t), 2.60 (1 H, m), 2.27 (1 H, m), 1.34 (3 H, s), 1.20 (1 H, d), 0.60 (3 H, s). ^{13}C NMR (500 MHz, CDCl_3) δ (ppm): 169.71, 166.43, 152.70, 134.58, 132.61, 127.44, 126.80, 125.31, 52.43, 48.10, 39.93, 38.90, 31.09,

30.51, 25.87, 21.18. MS: m/z 289.33 $[M+H]^+$. Anal. Calcd. for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.77; H, 7.01.

(1S,9S)-10,10-dimethyltricyclo[7.1.1.0^{2,7}]undeca-2,4,6-triene-5,6-phthalic acid (4). Compound **3** (870 mg, 3 mmol) was dissolved in 10 ml tetrahydrofuran and 10 ml 2 mol/L NaOH aqueous solution was added. The mixture was stirred for at 50 °C for 5 h, the organic solvent was removed under vacuum. 2 mol/L HCl was added dropwise until pH of aqueous solution became 2 ~ 3. The product was extracted with chloroform (10 ml \times 3) and washed with water and saturated salt water, dried by anhydrous sodium sulfate. The chloroform was evaporated and the product was dried in vacuum to get a yellow oil (588mg, yield: 74%). ¹H NMR (500MHz, CDCl₃) δ (ppm): 7.80 (1 H, d), 7.08 (1 H, d), 3.20 (2 H, m), 2.89 (1 H, t), 2.68 (1 H, m), 2.32 (1 H, m), 1.48 (3 H, s), 1.28 (1 H, d), 0.68 (3 H, s). ¹³C NMR (500 MHz, CDCl₃) δ (ppm): 175.27, 171.16, 153.48, 134.60, 132.46, 128.13, 126.92, 124.85, 48.33, 39.87, 38.95, 31.12, 30.69, 25.92, 21.27. MS: m/z 259.50 $[M]^-$. Anal. Calcd. for $C_{15}H_{16}O_4$: C, 69.22; H, 6.20. Found: C, 70.01; H, 6.14.

(1S,9S)-10,10-dimethyltricyclo[7.1.1.0^{2,7}]undeca-2,4,6-triene-5,6-phthalic anhydride (5). Compound **4** (5.16 g, 20 mmol) and 10 ml acetic anhydride were heated under gentle reflux for 5 h with slow distilling off acetic acid. After cooling, most of acetic anhydride was removed under vacuum. The solid was filtered and washed with petroleum ether. The residue was dried in vacuum to get a dark yellow solid (4.30 g, yield: 89%). ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.73 (1 H, d), 7.41 (1 H, d), 3.36 (2 H, m), 3.00 (1 H, t), 2.79 (1 H, m), 2.46 (1 H, m), 1.47 (3 H, s), 1.29 (1 H, d), 0.67 (3 H, s). ¹³C NMR (500 MHz, CDCl₃) δ (ppm): 163.26, 157.43, 137.60, 132.89, 128.89, 128.07, 123.30, 48.42, 39.47, 39.17, 31.46, 31.05, 25.95, 21.32. MS: m/z 243.50 $[M+H]^+$. Anal. Calcd. for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.07; H, 5.85.

(1S,9S)-10,10-dimethyltricyclo[7.1.1.0^{2,7}]undeca-2,4,6-triene-5,6-phthalic amide (6). Compound **5** (3.63 g, 15 mmol) was heated under stirring in formamide (10 ml) for 3 h under reflux. After cooling to room temperature, 20 ml water was added. The residue was filtered and washed with water and dried in vacuum to get a brown solid (3.43 g, yield: 95%). ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.98 (1 H, d), 7.60 (1 H, d), 3.36 (2 H, m), 2.94 (1 H, t), 2.75 (1 H, m), 2.41 (1 H, m), 1.45 (3 H, s), 1.29 (1 H, d), 0.68 (3 H, s). ¹³C NMR (500 MHz, CDCl₃) δ (ppm): 169.16, 168.10, 155.35, 135.59, 130.92, 130.62, 129.08, 121.14, 48.46, 39.68, 39.23, 31.64, 31.05, 26.05, 21.33. MS: m/z 240.50 $[M]^-$. Anal. Calcd. for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.81. Found: C, 74.37; H, 6.42; N, 5.77.

(1S,9S)-10,10-dimethyltricyclo[7.1.1.0^{2,7}]undeca-2,4,6-triene-5,6-phthalic diamide (7). Compound **6** (3.25 g, 13.5 mmol) was stirred for 48 h in 28% ammonia water in sealed flask at room temperature. The precipitate was filtered and washed with water and dried in vacuum to get a white solid (2.64 g, yield: 75%). ¹H NMR (500 MHz, DMSO-*d*₆) δ (ppm): 7.62 (1 H, d), 6.98 (1 H, d), 2.95 (2 H, m), 2.81 (1 H, t), 2.63 (1 H, m), 2.28 (1 H, m), 1.44 (3 H, s), 1.13 (1 H, d), 0.61 (3 H, s). ¹³C NMR (500 MHz, DMSO-*d*₆) δ (ppm): 170.92, 169.68, 149.14, 137.50, 132.07, 131.33, 125.60, 125.21, 47.69, 38.88, 31.51, 30.99, 26.19, 21.71. MS: m/z 259.33 $[M+H]^+$. Anal. Calcd. for $C_{15}H_{18}N_2O_2$: C, 69.74; H, 7.02; N, 10.84. Found: C, 69.70; H, 7.03; N, 10.84.

(1S,9S)-10,10-dimethyltricyclo[7.1.1.0^{2,7}]undeca-2,4,6-triene-5,6-phthalonitrile (8). Compound **7** (2.58 g, 10 mmol) was dissolved in 40 ml dimethyl formamide with stirring. The

mixture was cooled to -20 °C, and 20 ml thionyl chloride was added over a period of 20 ~ 30 minutes. After stirring for 2 h in 0 °C, the mixture was warmed to room temperature and stirring for 1 day. Then it was poured in 400 g ice, filtered washed with water for 3 times, and dried. The residue was dried in vacuum to get a pale solid (1.82 g, yield 82%). ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.54 (1 H, d), 7.27 (1 H, d), 2.92 (2 H, m), 2.77 (1 H, t), 2.45 (1 H, m), 1.46 (3 H, s), 1.24 (1 H, d), 0.65 (3 H, s). MS: m/z 223.50 $[M+H]^+$. ¹³C NMR (500MHz, CDCl₃) δ (ppm): 153.78, 142.08, 130.94, 130.05, 116.01, 114.77, 114.41, 112.75, 47.95, 39.57, 39.05, 32.81, 31.11, 25.71, 21.27. MS: m/z 223.50 $[M+H]^+$. Anal. Calcd. For $C_{15}H_{14}N_2$: C, 81.05; H, 6.35; N, 12.60. Found: C, 81.03; H, 6.38; N, 12.66.

(1S,9S)-10,10-dimethyltricyclo[7.1.1.0^{2,7}]undeca-2,4,6-triene-5,6-phthalocyaninatoeuropium (EuPc*₂). A mixture of phthalonitrile derivative **8** (222 mg, 1mmol), Eu(acac)₃·H₂O (75 mg, 0.16 mmol), 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) (0.15ml, 1 mmol), and 8 ml of n-hexanol was refluxed under Ar for 24 h. After cooling to room temperature, 10 ml mixed solvent of methanol/water (v/v = 1:1) was added in the mixture to precipitate the product. The dark green product was filtered off and washed with the mixed solvent. Finally, pure phthalocyanine derivative **EuPc*₂** was obtained as a dark blue solid by column chromatography on silica gel using dichloromethane/n-hexane as eluent (85 mg, yield: 35%). FT-IR ν_{max} (cm⁻¹): 2981, 2918, 2868, 1596, 1469, 1432, 1384, 1319, 1263, 1220, 1109, 1070, 916, 765. MS (MALDI-TOF): m/z 1930.75 $[M+H]^+$. Anal. Calcd. For $C_{120}H_{112}N_{16}Eu$: C, 74.67; H, 5.85; N, 11.61. Found: C, 74.40; H, 5.88; N, 11.66.

(1S,9S)-10,10-dimethyltricyclo[7.1.1.0^{2,7}]undeca-2,4,6-triene-5,6-phthalocyaninatoerbium (ErPc*₂). Compound **ErPc*₂** was prepared by the same procedure as that described for **EuPc*₂** by using compound **8** (222 mg, 1 mmol), Er(acac)₃·H₂O (77 mg, 0.16 mmol), 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) (0.15 ml, 1mmol), and 8 ml of n-hexanol in the reaction. The purification of **ErPc*₂** was achieved by column chromatography on silica gel using dichloromethane/n-hexane as eluent to get a dark green powder (50 mg, yield: 22%). FT-IR ν_{max} (cm⁻¹): 2921, 2853, 1632, 1467, 1437, 1384, 1365, 1320, 1263, 1219, 1102, 1070, 934,767. MS (MALDI-TOF): m/z 1945.85 $[M+H]^+$. Anal. Calcd. For $C_{120}H_{112}N_{16}Er$: C, 74.08; H, 5.80; N, 11.52. Found: C, 74.20; H, 5.77; N, 11.56.

(1S,9S)-10,10-dimethyltricyclo[7.1.1.0^{2,7}]undeca-2,4,6-triene-5,6-phthalocyaninatoluthetium (LuPc*₂). Compound **LuPc*₂** was prepared by the same procedure as that described for **EuPc*₂** by using compound **8** (222 mg, 1 mmol), Lu(acac)₃·H₂O (78 mg, 0.16 mmol), 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) (0.15 ml, 1 mmol), and 8 ml of n-hexanol in the reaction. The purification of **LuPc*₂** was achieved by column chromatography on silica gel using dichloromethane/n-hexane as eluent to get dark green powder (32 mg, yield: 14%). FT-IR ν_{max} (cm⁻¹): 2983, 2918, 2867, 1597, 1468, 1441, 1383, 1367, 1321, 1263, 1221, 1109, 1071, 915, 768. MS (MALDI-TOF): m/z 1952.73 $[M+H]^+$. Anal. Calcd. For $C_{120}H_{112}N_{16}Lu$: C, 73.79; H, 5.78; N, 11.47. Found: C, 73.76; H, 5.74; N, 11.46.

Electrochemical Measurements

Electrochemical measurements were carried out with a CHI600E electrochemical workstation utilizing a three-electrode cell configuration at 25 °C. For square wave voltammetry (SWV) measurement, the working electrode was a Pt disc with a surface area of 0.071 cm² or glassy carbon electrode. A Pt wire served as the counter electrode while saturated calomel electrode (SCE) was employed as the reference electrode.

Tetrabutylammonium perchlorate (TBAP) in DCM or DMF was used as the supporting electrolyte at a concentration of 0.1M. High purity Ar was used to remove dissolved O₂ for 15 min prior to each run and to maintain an Ar blanket during the measurements. *In-situ* spectroelectrochemical measurements were carried out by utilizing a three-electrode configuration of a thin-layer quartz spectroelectrochemical cell at 25 °C. The working electrode was a Pt semi-transparent electrode. A Pt wire counter electrode separated by a glass bridge and a SCE reference electrode separated from bulk of the solution by a double bridge were used.

The measurements of electrochromic properties were performed at room temperature on homogeneous thin films of LnPc*₂ molecules on indium-tin-oxide (ITO) coated glass substrates. The phthalocyanines were dissolved in cyclohexane in the concentration of 10 mg/ml for fresh use as the spreading solution in spin coating. The LnPc*₂ films were coated on ITO glasses by spin coating. The deposition of such films was accomplished by employing a KW-4A spin coater at 2000rpm for 30s. Thickness of the deposited films was characterized by AFM. Using the spun film coated ITO substrate as the working electrode, the electrochemical and electrochromic properties were investigated in a quartz cell containing a 0.1 M LiClO₄ aqueous solution as an electrolyte. A saturated calomel electrode (SCE) and a platinum sheet were used as the reference electrode.

Results and discussion

Synthesis and characterization

The bis(phthalocyaninato) rare earth complex LnPc*₂ (Ln = Eu, Er, Lu) were synthesized from the acetylacetonate lanthanide salts and (1S,9S)-10,10-dimethyltricyclo[7.1.1.0^{2,7}]undeca-2,4,6-triene-5,6-phthalonitrile (denoted as compound **8** as shown in Scheme 1). In contrast to the literature where the retro Diels-Alder reaction was commonly used to synthesize the functional phthalocyanines or naphthalocyanines,^[7] we prepared the phthalonitrile compound **8** from unsaturated aldehyde for the first time. Cyclotetramerization of the phthalonitrile **8** in the presence of Ln(acac)₃·H₂O (Ln = Eu, Er, Lu) gave the desired double-decker lanthanide phthalocyanine LnPc*₂. The dark green (for ErPc*₂ and LuPc*₂) or blue (for EuPc*₂) products were isolated by column chromatography on silica gel using petroleum ether/dichloromethane (4:1) as eluent. ¹H NMR spectra showed that there are various isomers mixed in the product. Unlike in the literature where higher or similar yields were observed for Ln(III) compounds with smaller central metal ionic radius, the yields declined sharply from Eu(III) compound to Lu(III) compound in our study. The decrease of yield might be attributed to the remarkable steric hindrance of the rigid ring on the macrocycles, which is different from the substituted groups (alkyl, alkoxy, phenoxy or macrocycle groups) with small steric hindrance. LnPc*₂ (Ln = Eu, Er, Lu) have excellent solubility in common solvents. The enhanced solubility could be attributed to both the decreased intermolecular interactions due to the bulky pinene groups and the existence of several isomers in these bis(phthalocyaninato) rare earth complex.

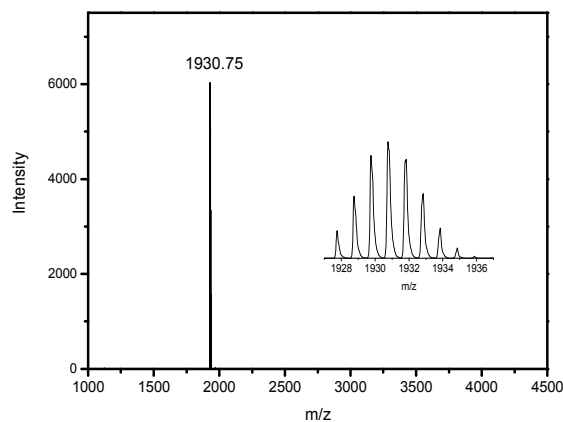


Figure 2. MALDI-TOF mass spectra of compounds EuPc*₂ with DHB as the matrix; isotopic patterns for the corresponding molecular ions are shown in insets.

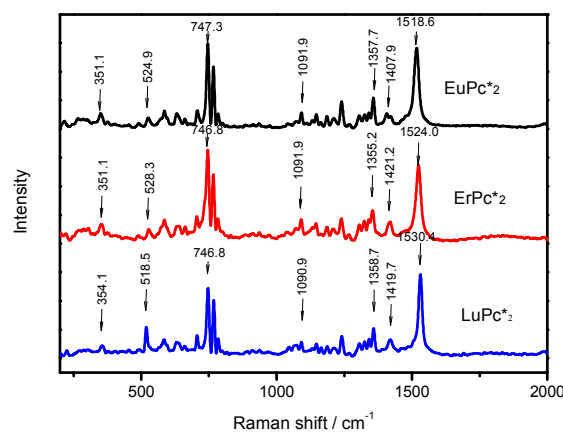


Figure 3. Raman spectra of LnPc*₂ (Ln = Eu, Er, Lu) at room temperature.

LnPc*₂ (Ln = Eu, Er, Lu) complex were characterized by MALDI-TOF, elemental analysis, FT-IR and Raman spectra. The MALDI-TOF mass spectra of LnPc*₂ (Ln = Eu, Er, Lu) with 2, 5-dihydroxybenzoic acid (DHB) as matrix revealed intense molecular ion peaks with characteristic isotopic patterns (Figure 2 and Figure S1 ~ S2). The results of elemental analysis are in accordance with the stimulated result, which indicates the purity of the phthalocyanines. The Raman spectra of LnPc*₂ (Ln = Eu, Er, Lu) at room temperature (Figure 3) show characteristic Raman shifts for typical lanthanide phthalocyaninato double-deckers.^[8] The vibrational frequencies in the range of 1300 ~ 1550 cm⁻¹ are assigned to isoindolyl ring stretching and the aza group stretching. Several peaks observed in the range of 1000 ~ 1300 cm⁻¹ are attributed to aromatic C-H bending. The bands at 550 ~ 700 cm⁻¹ correspond to Pc breathing. The low-frequency modes in the range of 200 ~ 530 cm⁻¹ are assigned to the metal-nitrogen stretching vibrations. The frequencies of vibration are found to increase with a decrease of the lanthanide ionic radius. Similar observations were reported for other LnPc₂ and can be attributed to the increase of the π-π interaction between two aromatic rings due to the decrease of the central metal ionic radius.^[9]

Absorption Spectra

The electronic absorption spectra of LnPc^*_2 (Ln = Eu, Er, Lu) are presented in Figure 4 (in dichloromethane for UV-Vis region) and Figure 5 (in carbon tetrachloride for NIR region). The data of the spectra are summarized in Table S2. All the bis-phthalocyanine complex LnPc^*_2 show strong N-bands at 300 ~ 304 nm and Soret bands at 329 ~ 364 nm region. The intense visible bands at 623 ~ 709 nm can be ascribed to the Q-bands of the macrocycles. Two π -radical related bands were observed at 504 ~ 525 (blue valence bands) and 932-945 nm (red valence bands), which could be attributed to $2e_g-a_{1u}$ and $1e_g-a_{1u}$ transitions, respectively, where the a_{1u} orbital represents an electron hole in one phthalocyanine ring.^[1b] The inter valence bands at 1620 ~ 1944 nm are due to electronic transitions from the second-highest occupied orbital to the semi-occupied orbital.^[10] Along with the decrease of ionic radius from Eu(III) to Lu(III), most of the absorptions, especially the longest-wavelength ring-to-ring bands (inter valence bands) shift hypsochromically, whereas the bands at 932 ~ 945 nm shift bathochromically. Such changes suggest the interaction between two rings weakened with the increase of the metal centres, and are in good accordance with preciously published data for bisphthalocyanine sandwich complex.^[11] The electronic circular dichroism (ECD) spectra of the new bisphthalocyanine rare earth complex containing chiral pinene groups were also investigated. As shown in Figure S4, a series of cotton effects were observed in the range of 300-800 nm, manifesting the chirality of LnPc^*_2 complexes.

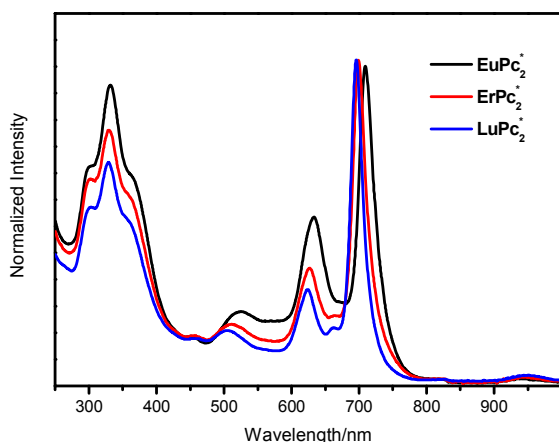


Figure 4. UV-Vis absorption spectra of LnPc^*_2 (Ln = Eu, Er, Lu) in dichloromethane.

Notably, the inter valence bands of LnPc^*_2 show apparent red shifts as compared with the published LnPc_2 derivatives.^[12, 13] To the best of our knowledge, the NIR absorptions of EuPc^*_2 , ErPc^*_2 , LuPc^*_2 are all the most red-shifted ones in comparison with other mononuclear Eu(III), Er(III) and Lu(III) double-decker phthalocyanines.^[3, 11, 12] Such a huge red-shift should be originated from the large steric hindrance of rigid pinene group which increases the intramolecular π - π distances between the macrocycles.

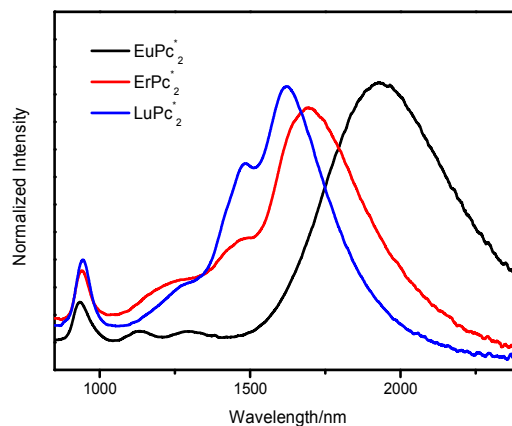


Figure 5. Near-IR absorption spectra of LnPc^*_2 (Ln = Eu, Er, Lu) in carbon tetrachloride.

Electrochemical properties

The electrochemical behavior of complex LnPc^*_2 were investigated in DCM/TBAP (-1 ~ 2 V) or DMF/TBAP (-2.8 ~ -1 V) electrolyte system by square-wave voltammetry with platinum disk electrode and glassy carbon electrode in the potential range of -2.8 ~ 2 V (vs. SCE). The half-wave redox potentials vs. SCE are summarized in Table 1. Within the electrochemical windows of DCM and DMF and according to the results of SWV, all the three complex LnPc^*_2 undergo at least five quasi-reversible reductions and two quasi-reversible oxidations, while an unexpected reduction as sixth reduction appeared for ErPc^*_2 . (Figure S5)

The characteristic electrochemical response of LnPc^*_2 is the redox couples R_1 at -0.044 ~ 0.060 V and Ox_1 at 0.352 ~ 0.436 V due to the reduction and oxidation of the radical Pc ring, respectively. As shown in Table 1, the redox potentials of both R_1 and Ox_1 are shifted to the cathodic side along the decrease of central metal ion radius, which is in agreement with previous works.^[11, 13] On the other hand, the redox potentials of Ox_2 were shifted slightly to the positive direction. Therefore, the values of $\Delta E^0_{1/2}$ and $\Delta E_{1/2}$ are increasing while that of $\Delta E^1_{1/2}$ are decreasing from Eu to Lu, which indicates an increase in π - π interaction.^[13c, 14] The potentials of R_2 , R_3 , and R_4 of the three of LnPc^*_2 are independent of the size of the central rare earth ions. The results are also corresponding to the previous work.^[11, 14]

Most of the redox potentials of LnPc^*_2 are significantly shifted to the cathodic side as compared to the nonsubstituted LnPc_2 .^[14] The effect of pinene group on the electrochemical properties is complicated. On one hand, the incorporation of the four electron-donating pinene groups onto each phthalocyanine ring makes the compounds easier to oxidize and harder to reduce, leading to lower oxidation and reduction half-wave potentials. On the other, the steric hindrance of the pinene groups will increase both the intra-molecular interaction between the phthalocyanine and decrease the π - π interaction, resulting in higher redox potential of Ox_2 , and lower redox potential of R_1 and Ox_1 .

Interestingly, in the electrochemical window of DMF with glassy carbon electrode as working electrode, we observed the sixth reduction couples R_6 at -2.690 V for ErPc^*_2 , which was

Table 1-1. Half-wave potentials (vs. SCE) for complex LnPc*₂.

Potential ^[a] /V	R ₆ ^[b]	R ₅ ^[b]	R ₄ ^[b]	R ₃ ^[b]	R ₂ ^[b]	R ₁	Ox ₁	Ox ₂	Ox ₃
EuPc*₂		-2.406	-2.122	-1.586	-1.234	0.060	0.436	1.354	1.630
ErPc*₂	-2.690	-2.292	-2.076	-1.596	-1.224	0.006	0.384	1.360	1.658
LuPc*₂		-2.408	-2.138	-1.598	-1.226	-0.044	0.352	1.420	1.732

^[a] Values versus Fc/Fc⁺ given in parentheses. ^[b] Measured in TBAP/DMF with glassy carbon electrode.

Table 1-2. Half-wave potentials (vs. SCE) for complex LnPc*₂.

Potential/V	$\Delta E_{1/2}^0$ ^[a]	$\Delta E_{1/2}$ ^[b]	$\Delta E_{1/2}^1$ ^[b]
EuPc*₂	0.376	0.918	1.294
ErPc*₂	0.378	0.976	1.230
LuPc*₂	0.398	1.068	1.182

^[a] $\Delta E_{1/2}^0 = Ox_1 - R_1$. ^[b] $\Delta E_{1/2} = R_1 - R_2$. ^[c] $\Delta E_{1/2}^1 = Ox_2 - Ox_1$.

unprecedented. According to the literature, only the cerium derivatives in the series of double-decker lanthanide(III) Pcs gives a metal-centered redox process,^[14, 15] thus this redox processes should also be ascribed to Pc ring-based electron transfer process.

Spectroelectrochemistry

The electrochemical sandwich-type lanthanide(III) phthalocyanines have been frequently observed to show significant changes in their absorption spectra while undergoing oxidation and reduction, and are thus promising electrochromic materials.^[15] It is also well documented that changing the substituent environments and metal center of these type of complex alters the redox properties which also affect the spectral and electrochromic features of the complex.^[15] Therefore, *in-situ* spectroelectrochemistry of the novel complex **LnPc*₂** were investigated in DCM/TBAP.

The UV/Vis spectral changes for complex **LnPc*₂** under controlled potential electrolysis at +0.8 V, -0.2 V and -1.4 V reflect transformation of neutral double-decker phthalocyanine into one and two-electron-oxidized and -reduced forms, respectively. As shown in Figure 6, for **EuPc*₂**, the band characterizing the radical form of the complex at 525 nm disappeared after the reduction reaction at -0.2 V, as one electron reduction of [**Pc*⁻¹Eu^{III}Pc*⁻²**] losses its radical character. At the same time, the Q band at 711 nm shifts to 706 nm with decreasing intensity and a strong band at 658 nm was detected. These results are in good agreement with those of [**Pc⁻¹Ln^{III}Pc⁻²**] / [**Pc⁻²Ln^{III}Pc⁻²**] process reported in previous literature.^[16] During the second reduction at -1.4 V, the bands at 658 nm decreases while a new band at 767 nm is recorded. Meanwhile, a new sharp band is recorded in 556 nm indicating radical formation after the second reduction reaction. During the first oxidation reaction, two new bands at 771 nm and 547 nm are recorded with the intensity decreased at 711 nm and 635 nm. These spectral changes are consistent with the spectral changes of typical sandwich type lanthanide(III) phthalocyanines.^[17] For **ErPc*₂** and **LuPc*₂**, similar spectra changes are also detected under potential. (Figure S6, S7)

Spectral changes in the NIR region are of special note. The spectroelectrochemistry studies were preformed in *o*-DCB containing 1M TBAP. Only **EuPc*₂** was investigated as the absorption of TBAP/*o*-DCB at ca. 1650 nm overlaps with the maximum peaks of **ErPc*₂** (1693 nm) and **LuPc*₂** (1620 nm) which obscures the spectral changes. During oxidation of the

neutral form of LnPc₂, a broad band with medium intensity appeared in the region between the red valence band and inter valence band. This band with maximum absorption at 1170 nm could be assigned to the nondegenerate HOMO-LUMO transition, which corresponds to the charge resonance of HOMO-SOMO excitation in the neutral form.^[18] Meanwhile, the intensity of the inter valence band at 1950 and red valence band at 932 nm decreased to almost no absorption. Combining the near-IR region absorption spectra before and after oxidation, the spectral changes cover almost all the NIR region from 800 to 2400 nm, which is unprecedented in the literature.^[8, 11, 12a, 19] Such features would be useful for application in near infrared electrochromic materials.

After completing reduction/oxidation, the initial neutral forms of the double-decker lanthanide complex were fully recovered by the back oxidation/reduction, which indicates the excellent stability of the **LnPc*₂**. As we know, the stability is an important factor for the electrochromic material. The detailed electrochromic properties were carried out as given blow.

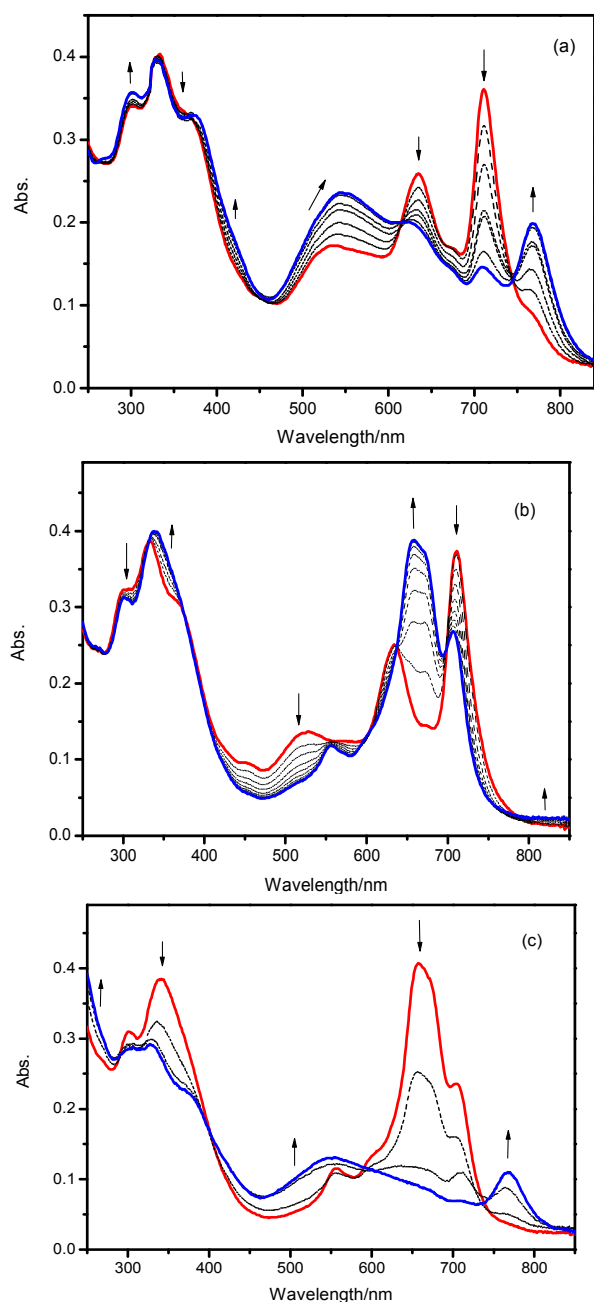


Figure 6. *In-situ* UV/Vis spectral changes of EuPc^*_2 in DCM containing 1M TBAP at (a) 0.8 V; (b) -0.2 V; (c) -1.4 V. (vs. SCE)

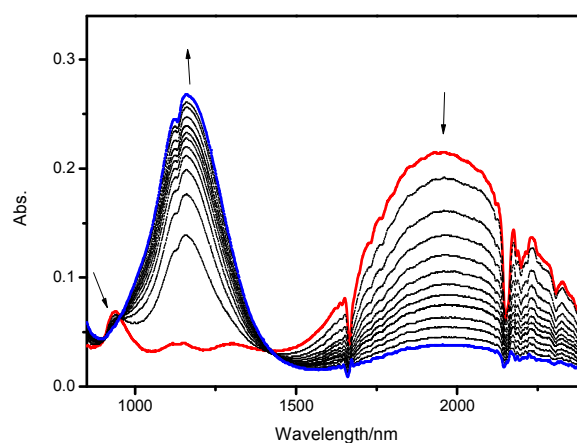


Figure 7. NIR spectral change of EuPc^*_2 in *o*-DCB containing 1M TBAP at +0.8 V (vs. SCE).

Electrochromic properties

To investigate the electrochromic features of LnPc^*_2 , the solid state electrochromic devices were fabricated. The excellent solubility of the LnPc^*_2 complex allow us to fabricated the devices through solution processable method. Therefore, thin films of the LnPc^*_2 complex were spun onto ITO coated glasses. Film thicknesses of the spun coated films were tested by AFM. The results showed that all the three LnPc^*_2 complex had thickness of 20~25 nm. Image of coated EuPc^*_2 film displays a very flat and compact surface (Figure 8b), indicating that the introduction of pinene groups can enhance the ability to form high quality phthalocyanines films on the surface of glass.

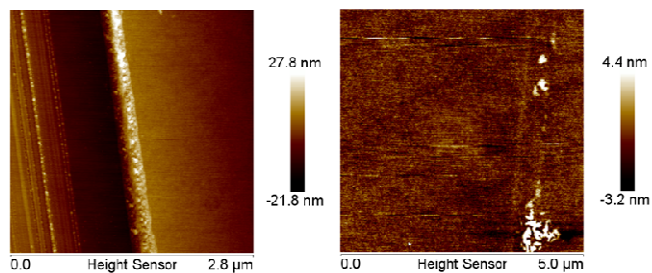


Figure 8. AFM images of EuPc^*_2 film.

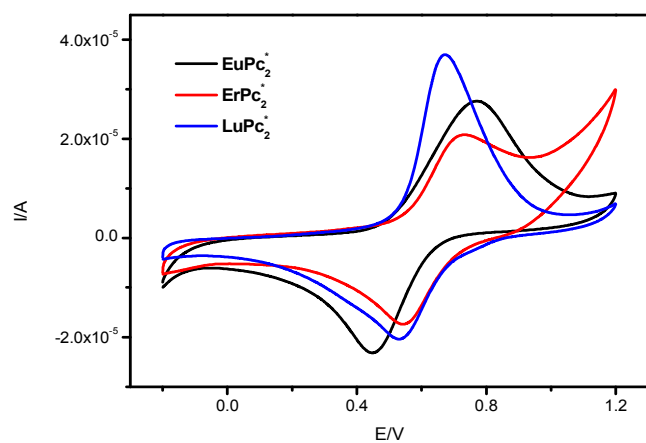


Figure 9. CV of $\text{LnPc}^*_2/\text{ITO}$ at a scan rate of 0.100 V/s in $\text{H}_2\text{O}/\text{LiClO}_4$ electrolyte system. (vs. SCE)

CV responses of the LnPc^*_2 films coated on ITO electrode with $\text{H}_2\text{O}/\text{LiClO}_4$ as electrolyte give one oxidation couples at 0.45–0.76 V (Figure 9). Without external potential application, $\text{LnPc}^*_2/\text{ITO}$ have green (blue) color. During the anodic potential scan, the color of the films turned to pink after wave of Ox_1 . During the reverse CV scan, its color changed to green (blue) again after the cathodic couple of Ox_1 process. The films were switched by repeating the potential steps using 0 V and +1.0 V with a residence time of 25 s in the electrolyte solution.

The optical contrast, reported as $\Delta T\%$ for characterizing the transmittance difference between the neutral state and oxidation state, was monitored as a function of time at the wavelength in the visible region.^[20] In order to investigate the $\Delta T\%$ of the films of LnPc^*_2 between 0 V and +1.0 V, the wavelengths of 538 nm (EuPc^*_2), 538 nm (ErPc^*_2), 534 nm (LuPc^*_2), 708 nm (EuPc^*_2), 700 nm (ErPc^*_2), 699 nm (LuPc^*_2) were chosen to be monitored. $\Delta T\%$ in the visible region at 538 nm and 708 nm were found to be 4.45% and 16.71% for EuPc^*_2 , while 4.69% at 538 nm, 19.07% at 700 nm for ErPc^*_2 and 6.2% at 534 nm, 26.9% at 699 nm for LuPc^*_2 .

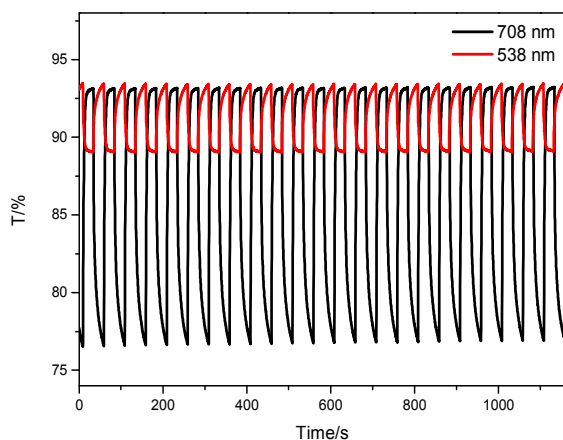


Figure 10. T% changes of $\text{EuPc}^*_2/\text{ITO}$ at two wavelengths versus time by repeating the potential steps using 0 V and +1.0 V with a residence time of 25 s in $\text{H}_2\text{O}/\text{LiClO}_4$ electrolyte system.

The coloration efficiency (CE) at different wavelength was listed in Table S3. The result shows that all the double-decker

complex have similar CE at similar wavelength in the same process. As mentioned before, stability of these complex is excellent. The T% stability losses were listed in Table 2, only tiny changes could be detected.

Table 2. Electrochromic parameters of $\text{LnPc}^*_2/\text{ITO}$ film in $\text{H}_2\text{O}/\text{LiClO}_4$ electrolyte system.

λ (nm)	E(V)	T% ^[a]	Responses time /s ^[b]	T% stability ^[c]	Optical contrast%
538	0.0	93.49	1.8	0.07	4.45
EuPc^*_2	+1.0	89.04	1.0	0.03	
708	0.0	76.44	1.5	0.30	16.71
EuPc^*_2	+1.0	93.15	1.3	0.05	
538	0.0	85.35	2.8	0.30	4.69
ErPc^*_2	+1.0	80.71	0.6	0.20	
700	0.0	66.76	2.2	0.75	19.07
ErPc^*_2	+1.0	85.83	0.4	0.18	
534	0.0	90.47	1.8	0.00	6.21
LuPc^*_2	+1.0	84.26	1.1	0.09	
699	0.0	63.67	1.2	0.59	26.89
LuPc^*_2	+1.0	90.56	1.4	0.10	

^[a] Maximum or minimum T% value reached at each potential switching. ^[b] Time needed to reach to the half of total %T change. ^[c] T% differences between the first and last switching step.

Conclusions

In summary, we have synthesized octa-pinene Double-decker lanthanide(III) phthalocyanines (EuPc^*_2 , ErPc^*_2 , LuPc^*_2) and studied their spectral, electrochemical, spectroelectrochemical and electrochromic properties. The steric hindrance of pinene groups not only enhances the solubility but also results in significant change in the spectral and electrochemical properties as compared to their unsubstituted counterparts. The inter valence band of LnPc^*_2 appears to be the most red-shifted absorption in comparison with the literature value of corresponding mononuclear double-decker lanthanide(III) ions phthalocyanines. By applying external voltages, the solution of LnPc^*_2 exhibit electrochromic behavior both in the UV-Vis and near-IR region. The spectra change of EuPc^*_2 covers almost all the range of NIR region. Due to the excellent solubility and film-forming ability of the new LnPc^*_2 complex, solution processable solid state electrochromic devices were fabricated. The electrochromic devices show reversible color change from green (blue) to pink during potential application of 0 V and 1 V, with high color efficiency and nice stability. Such features are very intriguing in wide applications like smart windows, displays, computer data storage, active optical filters, and thermal control (heat gain or loss) in buildings and spacecrafts.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Additional characterization data. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

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Graphic Abstract

The introduction of pinene groups into lanthanide(III) double-decker phthalocyanine results in excellent solubility as well as nontrivial spectral and electrochemical properties. Upon external potential, the new lanthanide(III) double-decker phthalocyanine complexes show electrochromic properties at both visible and near infrared range. The spectra change of **EuPc*₂** covers almost all the range of NIR region with two distinct part (900 ~ 1420 nm and 1420 ~ 2400nm).

