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Sandwich Complexes

# First Example of Nonlinear Optical Materials Based on Nanoconjugates of Sandwich Phthalocyanines with Quantum Dots

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**Abstract:** We report original, selective, and efficient approaches to novel nonlinear optical (NLO) materials, namely homoleptic double- and triple-decker europium(III) complexes **2** and **3** with the $A_3B$-type phthalocyanine ligand (2,3-bis[2′-(2′′-hydroxyethoxy)ethoxy]-9,10,16,17,23,24-hexa-*n*-butoxyphthalocyanine **1**) bearing two anchoring diethyleneglycol chains terminated with OH groups. Their covalently linked nanoconjugates with mercaptosuccinic acid-capped ternary CdSeTe/CdTeS/ZnSe quantum dots are prepared in the presence of an ethyl(dimethylaminopropyl)carbodiimide activating agent. Optical limiting (OL) properties of the obtained low-symmetry complexes and their conjugates with quantum dots (QDs) are measured for the first time by the open-aperture Z-scan technique (532 nm laser and pulse rate of 10 ns). For comparison, symmetrical double- and triple-decker $Eu^{III}$ octa-*n*-butoxyphthalocyaninates **5** and **6** and their mixtures with trioctylphosphine oxide-capped QDs are also synthesized and studied. It is revealed that both lowering of molecular symmetry and expansion of the π-electron system upon moving from double- to triple-decker complexes significantly improves the OL characteristics, making the low-symmetry triple-decker complex **3** the most efficient optical limiter in the studied family of sandwich complexes, affording 50% lowering of light transmittance below 0.5 J cm$^{-2}$ input fluence. Conjugation (both covalent and noncovalent) with QDs affords further enhancement of the OL properties of both double- and triple-decker complexes. Altogether, the obtained results contribute to the development of novel nonlinear optical materials for future nanoelectronic and optical device applications.



## Introduction

Metallophthalocyanines (MPcs) have gained pivotal attention in the development of suitable and efficient nonlinear optical (NLO) limiting devices with large nonlinear absorption (NLA) coefficients and inherent fast response times, owing to their excellent photophysical properties associated with their extended aromatic π-electron system.[1–10] It has been suggested that lanthanide double-decker phthalocyaninates ($LnPc_2$, DD) show improved optical nonlinearities because of their expanded π-electron system and the presence of the heavy lanthanide central metal,[11–16] which enhances the rate of intersystem crossing (ISC) to the triplet state.[17,18] A further increase in the number of decks from two to six has been shown to enhance optical-limiting behavior,[19,20] although these studies are still limited: in the case of triple-decker sandwiches ($Ln_2Pc_3$, TD), only a few studies have been reported, including homoleptic trisphthalocyaninates[21,22] and some heteroleptic complexes.[23–25] Unlike the DD counterparts, which are paramagnetic, the positive charge on the two $Ln^{III}$ ions in TD complexes balances the negative charge in the three Pc ligands, thus improving the NLO behavior.

On the other hand, semiconductor quantum dots (QDs) have found applications in diverse areas including biomedical research and optical devices owing to their high molar extinction coefficients, broad absorption and narrow emission spectra, and size tunability.[26–28] The NLO behavior of Pcs linked to QDs has been exploited,[29] revealing a significant improvement in NLO properties in comparison with those of unbound Pcs. However, the grafting of sandwich complexes onto QDs and NLO studies of the resulting conjugates has never been done before.

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