Synthesis of New Monoporphyrinato Lanthanide Complexes for Potential Use in Optical Limiting

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Three monoporphyrinato lanthanide complexes based on 5,10,15,20-tetrakis(*p*-diphenylaminophenyl)-21*H*,23*H*-porphine (H_2TDPAPP) were synthesized, and experimental investigations of the nonlinear optical transmittance characteristics at 532 nm show that they are excellent optical limiters with performance comparable or superior to those of the reverse saturable absorption dyes such as fullerene C_{60} and metal phthalocyanine complexes.

With the rapid development of laser technology, the damage to human eyes, optical sensors, and sensitive optical components caused by exposure to sudden intense laser pulses has driven much effort in the search for effective optical limiters that possess fast response speeds and relatively high linear transmissions.[1] Optical limiters are materials that are transparent at normal light intensities while opaque to very bright light.[2]

At present, materials practically employed for optical limiting are largely small molecules, such as fullerene,[3] phthalocyanines,[4] diacetylenes,[5] nanotubes,[6] and organometallic compounds.[7] Metalloporphyrins are among the most effective optical limiters,[8] which achieve optical limiting by a mechanism known as reverse saturable absorption.[9] Wang and his co-workers have reported a series of pentaazadentate porphyrin-like metal complexes used in optical-limiting materials, where the metal ion is Sm^{3+} or Gd^{3+}.[10] In this paper, we describe the first report on a series of monoporphyrinato lanthanide complexes (TDPAPP)Ln(L_{OMe}) (Ln = Yb, Er, and Gd) with large optical-limiting capabilities (Chart 1).

The porphyrin free base (H_2TDPAPP) was prepared according to the literature method by condensation of pyrrole and 4-diphenylaminobenzaldehyde.[11] Treatment of an excess of $Ln[N(SiMe_3)_2]_3 \cdot x[LiCl(THF)_3]$ (Ln = Yb, Er, or Gd), generated from the reaction of anhydrous $LnCl_3$ with 3 equiv of $Li[N(SiMe_3)_2]$ in tetrahydrofuran (THF), with porphyrin free base under nitrogen in refluxing toluene for 12 h, followed by addition of excess NaL_{OMe} to the reaction mixture at room temperature, gave green crystals of (TDPAPP)Ln(L_{OMe}) (Ln = Yb **1**,[12] Er **2**,[13] or Gd **3**[14]) in about 80% yield. The tripodal anion, L_{OMe}^- ($L_{OMe}^- = (\eta^5\text{-}C_5H_5)Co[P(=O)(OMe)_2]_3^-$), is capable of shielding the lanthanide ion from interactions with the environment.

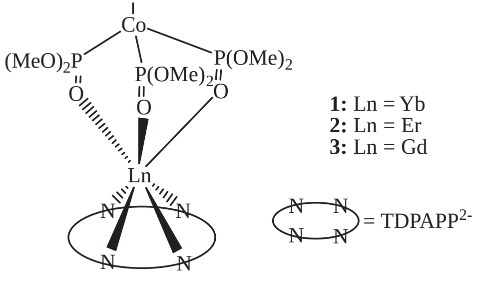

Chart 1.

An ideal material for optical limiting would have low ground-state absorption over a wide spectral bandwidth and strong excited-state absorption across the same region.[2] The UV–vis spectra of the complexes taken in toluene at room temperature are shown in Figure 1. Clearly, there is a transparent window at 532 nm for the monoporphyrinato lanthanide complexes.

To study the optical-limiting properties, the intensity-dependent transmittance and *Z*-scan measurements were performed with a Q-switched Nd:YAG laser with an output wavelength of 532 nm. From the *Z*-scan curves for the three lanthanide complexes measured in CH_2Cl_2 (Figure 2), all of them show excellent optical-limiting behavior. When the sample is far from the focus ($Z/Z_0 = 0$) and the incident irradiance upon it is weak, the transmittance of the sample remains almost constant and shows a linear optical property. But when the sample is close to the focus and the incident irradiance is strong, the transmittance of the sample decreases and the optical-limiting effect appears. It is clearly that complex **2** shows the strongest optical-limiting capability, and the property is superior to that of C_{60}, which was considered as an excellent optical limiter. The complexes **1** and **3** also exhibit good optical-limiting properties, which are comparable to that of C_{60}. The optical-limiting thresh-

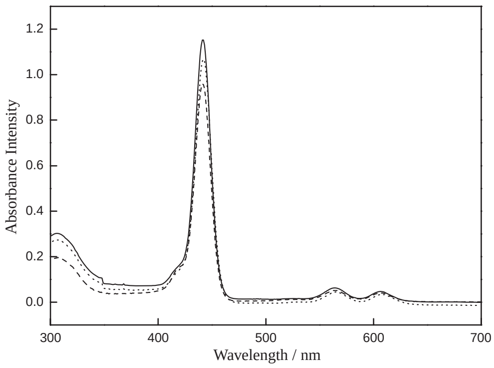

Figure 1. UV–vis linear-absorption spectra of **1** (solid line), **2** (dashed line), and **3** (dotted line) in dilute toluene solutions at room temperature.

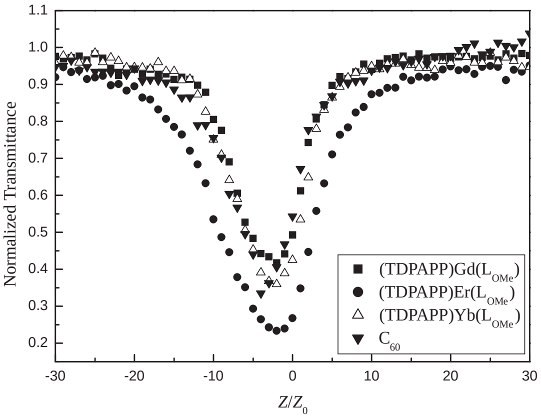

Figure 2. Open aperture *Z*-scan results for the three monoporphyrinato lanthanide complexes and C_{60} solutions at the same linear transmittance of 82%.

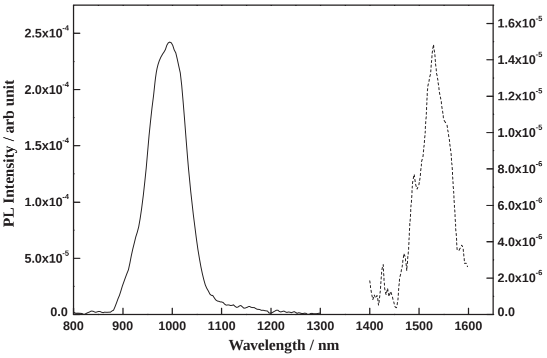

Figure 3. NIR luminescence spectra of **1** (solid line) and **2** (dashed line) in toluene upon excitation at 512 nm.

olds for these complexes range from 0.09 to 0.30 J/cm^2 at 82% linear transmittance.

The substitution of heavy metal in the porphyrin core can modify the spectral features by perturbing the ring π-electron system and can introduce several low-lying states in the HOMO–LUMO gap.[8d] It is well known that insertion of the lanthanide ion closely in the porphyrin core can make the energy of the triplet state of the ligand-transfer efficiently to the excited state of the metal ion and enable the ion to emit light in the near-infrared (NIR) region (Figure 3),[15] which would play the major role in achieving optical-limiting effects. Short excited-state lifetimes for the complexes (less than 4 ns measured at room temperature in toluene with the excitation wavelength at 337 nm) can verify the rapid charge transfer from the excited porphyrin to the lanthanide ions.[16] The complex **2** shows stronger optical-limiting capability than that of **1** and **3**, which can be attributed to much more low-lying excited states that Er(III) ion provides.[15]

In this work, we report the synthesis of three new monoporphyrinate lanthanide complexes that exhibit excellent optical limiting for a nanosecond laser pulse at 532 nm and these complexes are attractive candidates for optical-limiting materials.

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12 **1**: Green crystals; yield 75%. IR (KBr): 3445 (m), 2940 (m), 1591 (s), 1490 (s), 1276 (m), 1143 (s), 1006 (m), 752 (m), 696 (m) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 16.39 (s, 4H, Ar), 15.57 (s, 8H, β-H), 10.30 (s, 4H, Ar), 8.58–8.56 (m, 24H, Ar), 8.11–8.07 (m, 16H, Ar), 7.63–7.61 (m, 8H, Ar), 6.44 (s, 18H, OMe), −4.71 (s, 5H, η^5-C_5H_5). ^{31}P NMR (400 MHz, CDCl$_3$): δ 68.29 (s). UV–vis data in toluene, 20 °C, λ_{max}/nm [log(ε/dm^3 mol^{-1} cm^{-1}) in parentheses]: 441 (5.76), 564 (4.50), 607 (4.38). ESI–HRMS (+ mode, in CHCl$_3$) *m*/*z*: 1906.4548 {[M + H]$^+$, $C_{103}H_{88}CoN_8O_9P_3Yb$ requires 1906.4627}.

13 **2**: Green crystals; yield 81%. IR (KBr): 3445 (m), 2940 (m), 1591 (s), 1490 (s), 1277 (s), 1141 (s), 1006 (s), 796 (m), 752 (m), 696 (m) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 45.59 (s, 4H, Ar), 35.09 (s, 8H, β-H), 20.64–19.99 (m, 24H, Ar), 12.56 (s, 18H, OMe), 12.14 (s, 4H, Ar), 10.39 (s, 16H, Ar), 9.43 (s, 8H, Ar), −34.16 (s, 5H, η^5-C_5H_5). ^{31}P NMR (400 MHz, CDCl$_3$): δ −166.01 (s). UV–vis data in toluene, 20 °C, λ_{max}/nm [log(ε/dm^3 mol^{-1} cm^{-1}) in parentheses]: 441 (5.68), 564 (4.41), 606 (4.31). ESI–HRMS (+ mode, in CHCl$_3$) *m*/*z*: 1899.4461 {M$^+$, $C_{103}H_{87}CoN_8O_9P_3Er$ requires 1899.4488}.

14 **3**: Green crystals; yield 76%. IR (KBr): 3449 (m), 2940 (m), 1591 (s), 1491 (s), 1277 (m), 1137 (s), 1006 (m), 752 (m), 696 (m) cm^{-1}. UV–vis data in toluene, 20 °C, λ_{max}/nm [log(ε/dm^3 mol^{-1} cm^{-1}) in parentheses]: 442 (5.73), 566 (4.35), 608 (4.24). ESI–HRMS (+ mode, in CHCl$_3$) *m*/*z*: 1890.4455 {[M + H]$^+$, $C_{103}H_{88}CoN_8O_9P_3Gd$ requires 1890.2683}.

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