Supporting Information

Optical nonlinearities and photophysicochemical behaviour of green and blue forms of lutetium bisphthalocyanines

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Equipment

Infrared spectra were recorded on a Perkin Elmer 100 ART FT-IR spectrometer. Ultraviolet-visible spectra (UV-Vis) were measured on a Shimadzu UV-Vis 2550 spectrophotometer. The time-resolved phosphorescence decay of singlet oxygen at 1270 nm was used to determine singlet oxygen quantum yield in DMF. For these studies an ultra-sensitive germanium detector (Edinburgh Instruments, EI-P) was combined with a 1000 nm long pass filter (Omega, RD 1000 CP) and a 1270 nm band-pass filter (Omega, C1275, BP50) as described before [1]. ^{1}H NMR nuclear magnetic resonance signals were recorded on a Bruker AMX 600 NMR spectrometer. Elemental analyses were carried out on a Vario EL III MicroCube CHNS instrument. Analyzer.

All Z-scan experiments described in this study were performed using a frequency-doubled Nd:YAG laser (Quanta-Ray, 1.5 J /10 ns fwhm pulse duration) as the excitation source. The laser was operated in a near-Gaussian transverse mode at 532 nm (second harmonic), with a pulse repetition rate of 10 Hz and energy range of 0.1 µJ – 0.1 mJ. The low repetition rate of the laser prevents cumulative thermal nonlinearities. The beam was spatially filtered to remove the higher order modes and tightly focused with a 15 cm focal length lens. The liquid samples were placed in a cuvette (internal dimensions: 2 mm × 10 mm × 55 mm, 0.7 mL) with a pathlength of 2 mm (Starna 21-G-2).

Laser flash photolysis experiments were performed with light pulses produced by a Quanta-Ray Nd:YAG laser providing 400 mJ, 9 ns pulses of laser light at 10 Hz, pumping a Lambda-Physik FL3002 dye laser (Pyridin 1 dye in methanol). Details have been provided previously [2].

Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker EPR 300E X-band (10 GHz) spectrometer equipped with a TM probe with a flat quartz cell. The spin Hamiltonian parameters were obtained by simulation of the spectra. The static field (3462-3465 G), center field (3488-3495 G), modulation amplitude (6.25-6.38 G), time constant (10.24 msec), conversion time (5.12 msec), resolution (1024 pts), power (2.00mW), modulation frequency (100 kHz) and center field (51.29-57.93 G) were used as the experimental parameters at 298 K.

Triplet state quantum yields

Triplet state (Φ_T) quantum yield of complex **2** was calculated using comparative methods that have been described previously [27], using ZnPc in DMSO as a standard: $\Phi_T^{Std} = 0.65$ [3].

Singlet oxygen quantum yields

Singlet-oxygen quantum yields can be readily determined for for metallophthalocyanines by using the singlet-oxygen luminescence method (SOLM) in the presence and absence of a singlet-oxygen quencher such as sodium azide. The SOLM method involves the time-resolved phosphorescence decay of singlet oxygen at 1270 nm [4]. The dynamic course of $O_2(^1\Delta_g)$ concentration $[O_2(^1\Delta_g)]$ can be monitored and recorded, using Eq 1 as has been described in literature [5]

$$I(t) = B \frac{\tau_D}{\tau_T - \tau_D} [e^{-t/\tau_T} - e^{-t/\tau_D}] \qquad (1)$$

where I(t) is the phosphorescence intensity of singlet oxygen ($O_2(^1\Delta_g)$) at time t, τ_D is the lifetime of $O_2(^1\Delta_g)$ phosphorescence decay, τ_T is the triplet state lifetime of standard or sample and B is a coefficient involved in sensitizer concentration and singlet

oxygen quantum yield. The singlet oxygen quantum yield (Φ_Δ) of the phthalocyanine is then determined by a comparative method using Eq. 2:

$$\Phi_\Delta = \Phi_{\Delta(Std)} \cdot \frac{B \cdot OD^{Std}}{B^{Std} \cdot OD} \qquad (2)$$

where $\Phi_{\Delta(Std)}$ is the singlet oxygen quantum yield for the unsubstituted zinc phthalocyanine standard in DMF ($\Phi_{\Delta(Std)} = 0.56$ [6]). B and B^{Std} refer to coefficient involved in sensitizer concentration and $^1O_2$ quantum yield for the sample and standard respectively, and OD and OD_{Std} are the optical densities of the sample and standard at the excitation wavelength.

Nonlinear optical parameters

Devices such as optical limiters or saturable filters exhibit optical limiting effects when the intensity of the light beam is strongly attenuated, once the input intensity exceeds a threshold value (I_{lim}). The latter is determined by the characteristics of the system interacting with the beam, and represents critical parameters for the evaluation of the optical limiting (OL) properties of the device. Using nonlinear regression technique, all aperture z-scan data were fitted with the Eq. 3, where the normalised transmittance ($T_{Norm}(z)$) is defined as a function of position z [7]:

$$T_{Norm}(z) = \frac{1}{1 + \beta_2 L_{eff} \left(\dfrac{I_0}{1 + (z/z_0)^2} \right)} \qquad (3)$$

β_2 and I_0 are the effective intensity dependent nonlinear absorption coefficient and the intensity of the beam at focus, respectively. L_{eff} is the effective thickness of the sample and is given by Eq. 4 [8]. z and z_0 are sample position with respect to the input intensity and Rayleigh length, respectively.

$$L_{eff} = \frac{1 - e^{-(\alpha L)}}{\alpha} \qquad (4)$$

α and L are the linear absorption coefficient and the thickness of the sample respectively. α may be determined using Eq. 5:

$$\alpha = \frac{h\nu}{N} \beta_2 \qquad (5)$$

where h is Planck's constant and ν the frequency of a laser excitation. N is defined as the system's number of active species per unit volume ($N = N_A C$, N_A = Avogadro's number and C = sample concentration).

The imaginary component of the third order optical susceptibility $Im[\chi^{(3)}]$ is directly proportional to β_2, Eq. 6 [9]:

$$Im[\chi^{(3)}] = \frac{(n^2 \varepsilon_0 c \lambda \beta_2)}{(2\pi)} \qquad (6)$$

where c and n, respectively, are the speed of light in vacuum and the linear refractive index of the system. ε_0 is the permittivity of free space and λ is the wavelength of the laser light.

At a molecular level, there is a direct correlation of $Im[\chi^{(3)}]$ with the hyperpolarizability γ (which provides the nonlinear absorption per mole of the sample), Eq. 7 [9,10]:

$$\gamma = \frac{Im[\chi^{(3)}]}{C N_A f^4} \qquad (7)$$

where C is the concentration of active species in the triplet state, f represents Lorenz local field factor and is given by Eq. 8:

$$f = \frac{n^2 + 2}{3} \qquad (8)$$

The threshold intensity values, I_{lim} may be obtained from Eq. 9 [10]:

$$I_{\lim} = \frac{h\nu}{2\pi\sigma_s\tau_T} \qquad (9)$$

where σ_S and τ_T are the singlet state absorption cross section and triplet lifetime, respectively. An ideal optical limiter should have a low $I_{\lim}$ value because if it is too high, it becomes less reliable in terms of protection of sensitive optical elements.

The model for reverse saturable absorption of an optically active polyacene-based oligomer has been explained by Kojima et al [11], with the incident laser intensity (I_{in}) and the transmitted laser intensity (I_{out}) obeying Eq. 11:

$$\ln(\frac{I_{in}}{I_{out}}) = k(I_{in} - I_{out}) + A \qquad (10)$$

where k is a constant that depends on the absorption cross sections and lifetimes of the ground, excited-singlet, and excited-triplet states, while A is the absorbance of the ground state.

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