

Excited state properties of monomeric and dimeric axially bridged indium phthalocyanines upon UV–Vis laser irradiation†

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This contribution presents a series of results from different photophysical experiments realized at both resonance and off-resonance conditions on a group of newly synthesized cofacial bridged phthalocyanines. The most relevant aspect of the present study is the identification of a common photoexcited state, which can be reached by the same compound *via* two substantially different irradiation pathways.

The results of a study on the photophysical properties of a series of indium phthalocyanine (Pc) complexes R_4PcInX [$R = tert$ -butyl (*t*Bu) and $X = Cl$ (**1**) or *p*-trifluoromethylphenyl (*p*-TMP) (**2**)], $(R_4PcIn)_2L$ [$R = tBu$ and $L = 2,3,5,6$ -tetrafluorophenylene (TFP) (**3**)], and $(R_4PcInX)_2L$ [$X = Cl$ (**4**) or *p*-TMP (**5**) with $L = 1,4$ -diisocyanobenzene (dib)] (Fig. 1), are reported. The analysis of both linear and nonlinear optical (NLO) properties of these systems in the visible range has allowed the identification of defined photoexcited states which can be formed *via* high-intensity irradiation (in the order of 10^9 W m⁻²) at off-resonance as well as resonant frequency with respect to the linear optical spectrum of Pc's. The formation of defined photoexcited states in these Pc's by means of either off-resonance or resonant modes of irradiation is associated with the presence of the extended network of conjugated π -electrons which are highly polarizable and give rise to several transitions in the visible range from ground and excited states.¹ The importance of such findings relies on the definition of conditions of irradiation like optical field frequency and intensity regimes (linear or nonlinear), at which specific excited states of the indium Pc's are produced. Axial substitution in Pc complexes provokes relevant changes on the electronic structure of the molecule by altering the π -electronic distribution due to the dipole moment of the central

metal–axial ligand bond.^{2,3} This has been verified with axially substituted titanium,³ gallium and indium $PcMX's^2$ in which axial substitution affects the NLO properties through the alteration of the electronic hyperpolarizability.^{2,3} The novel axially bridged bis-phthalocyanines [*t*Bu₄PcIn]₂(TFP) (**3**), [*t*Bu₄PcInCl]₂-dib (**4**) and [*t*Bu₄PcIn(*p*-TMP)]₂-dib (**5**) (Fig. 1), were derived upon dimerization of *t*Bu₄PcInCl (**1**) and *t*Bu₄PcIn(*p*-TMP) (**2**) *via* reactions with the bidentate ligands dib¹ and TFP. When compared with the parent monomers **1** and **2**, the dimers **3–5** display linear UV–Vis spectra characterized by a blue-shift of the Q band in the order of 5–10 nm. Upon excitation with nanosecond laser pulses at 355 nm, *i.e.* roughly at the center of the B band (Fig. 2, lower panel), the observed transient absorption spectra of **1–5** in toluene are similar (see example of dimer **5** in Fig. 2). The transient absorption bands of **1–5** are centered at 520 nm^{2b} and accompany the disappearance of absorption in correspondence of the Q-band at 700 nm. The main excited state absorption is attributed to a triplet–triplet (T–T) transition corresponding to the transition from the lowest triplet excited state to the upper triplet excited states of the Pc's.⁴ From the analysis of the decays of the T–T absorption at 520 nm, the lifetimes of the triplet excited states (τ_T) were evaluated to be within the broad range $20 < \tau_T < 50$ μ s (Table 1). One of the reasons for the deactivation of the triplet excited states of **1–5** in

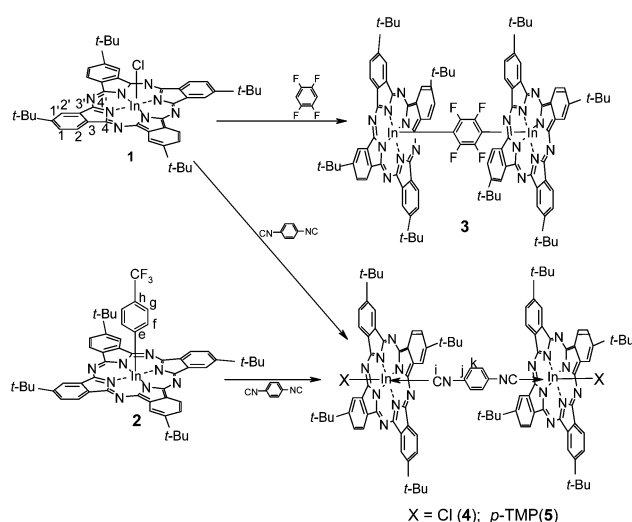


Fig. 1 Compounds 1–5.

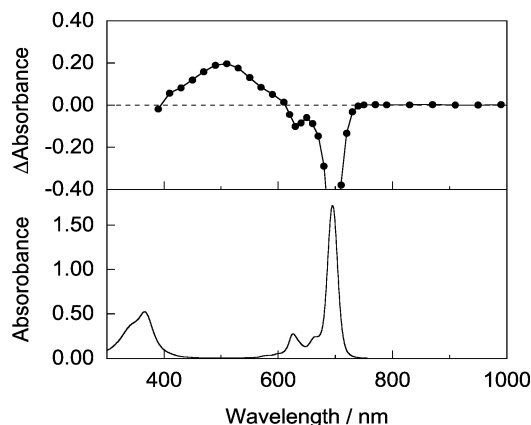


Fig. 2 UV–Vis linear absorption spectrum (lower panel) and transient absorption spectrum (upper panel) of **5** taken 100 ns after excitation with 355 nm laser pulse (pulse duration: 5 ns) in deaerated toluene.

Table 1 Excited states properties of **1–5** (τ_T : triplet-state lifetime; k_{TT} : T–T annihilation rate constant; τ_f : fluorescence lifetime at emission peak wavelength)

	τ_T/μ s	k_{TT}/mol^{-1} $\text{dm}^3 \text{s}^{-1}$	τ_f/ps
1	46	6.5×10^8	470
2	22	4.5×10^8	280
3	35	6.2×10^8	350
4	38	2.3×10^8	470
5	33	3.0×10^8	400

† Electronic supplementary information (ESI) available: experimental details and characterization data. See <http://www.rsc.org/suppdata/cc/b3/308677a/>

deaerated solutions was the occurrence of T–T annihilation as previously verified in analogous bridged Pc's (bimolecular T–T annihilation rate constants k_{TT} for 1–5 are given in Table 1).⁵ It is generally observed that indium Pc's with ligands possessing a stronger electron-withdrawing (EW) character, e.g. Cl in 1 and 4, or TFP in 3, have longer triplet excited state lifetimes.⁶ Upon dimerization an increase of the triplet state lifetime τ_T is also observed in passing from 2 to 5 (Table 1). In presence of oxygen, the lifetime of the triplet excited state is generally shortened for 1–5 as verified by the acceleration of the decay for the absorption band centered at 520 nm. This would indicate the quenching of Pc's triplet state by oxygen. Considering a bimolecular mechanism for the process of Pc triplet state quenching with oxygen, as well, a value of the rate constant $k_{O_2}^T$ in the order of $2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ was estimated for 1–5.⁴ Upon irradiation at 355 nm with continuous laser (linear optical regime), fluorescence peaks of the dimers 1–5 are observed in the range 700–710 nm, which correspond to the mirror image of the Q-bands having Stokes shifts in the order of 10 nm. For 1–5 the fluorescence decay profiles follow an exponential law with the fluorescence lifetimes (τ_f) ranging in the interval $250 < \tau_f < 500 \text{ ps}$ (Table 1). The variation of τ_f with the complex structure resembles what has been observed for τ_T , i.e. those complexes with ligands having a stronger electron-withdrawing character have longer fluorescence lifetimes. Moreover, dimerization produces the same effect on τ_T when 2 and 5 are compared.

Nonlinear off-resonance irradiation of dimers 3–5 at 532 nm with nanosecond pulses produces the effect of reverse saturable absorption⁷ as determined by Z-scan experiments (Fig. 3).⁸ Such an effect is a consequence of the increase of absorbance of 3–5 in the triplet excited state^{2b} in the optical window comprised between Q- and B-bands, as verified upon laser irradiation with ns pulses at 355 nm (Fig. 2, upper panel). This implies that both resonance and off-resonance irradiation of 3–5 with ns pulses generate analogous excited states whose absorptivity is larger than in the ground state in the spectral window comprised between the Q- and B- bands. The higher optical limiting (OL) effect from dimers 4 and 5 with respect to 3 (Fig. 3) at 532 nm indicates that the sharing of the axial

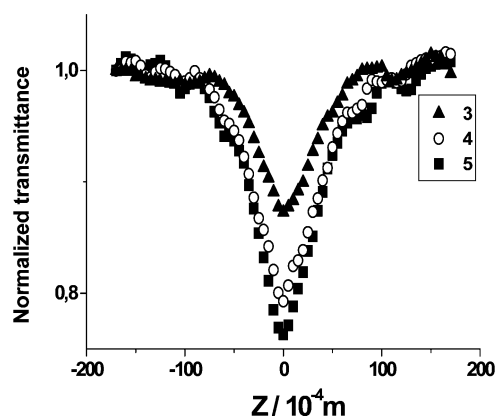


Fig. 3 Z-Scan profiles of compounds 3–5 at 532 nm. On the x -axis Z represents the distance of the sample from the focus of a gaussian beam. Laser intensity I varies with Z according to the relationship: $I(Z) = E/\tau w^2(Z)\pi$ where E , τ and $w(Z)$ are, respectively, the pulse energy, the pulse duration and the beam radius as a function of the distance from the focus Z ($w = 5 \text{ mm}$ at $Z = \pm 200 \times 10^{-4} \text{ m}$). At the focus I ranged in the interval $5\text{--}10 \times 10^{12} \text{ W m}^{-2}$.

ligand in the structure of dimer 3 reduces the absorption cross-section of the excited state producing the OL effect.⁹ In fact, the variations of τ_T in 3–5 cannot be responsible for the observed differences in the OL behavior of 3–5 since τ_T is always much longer than pulse duration (Table 1). The better OL performance of 4 and 5 with respect to monomers 1, 2 (not shown here)^{2b} and dimer 3, shows the favourable effect of Pc's dimerization on OL when the bridging ligand L coordinates the two Pc rings without replacing the pre-existing axial ligand X , like in 4 and 5. This finding is probably related to a lower extent of intermolecular aggregation for 4 and 5,¹⁰ as corroborated by the lower values of k_{TT} for 4 and 5 (Table 1). These features would favour the maintenance of the OL active state for 4 and 5 in a larger range of concentrations,^{2b,10} and indicate the poor electronic interaction between the bridged macrocycles.

In conclusion, we have demonstrated that irradiation of dimeric indium phthalocyanines at both resonance and off-resonance wavelengths in the nonlinear regime can lead to the generation of the same electronic excited state characterized by an increase of absorption in the optical window between the characteristic Q- and B- bands of Pc's. Such an alteration can be exploited for OL, which is more pronounced for dimeric structures displaying a reduced level of aggregation.

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