

Charge Transfer Photophysics of Tetra(α -amino) Zinc Phthalocyanine

Xian-Fu Zhang · Xijiang Li · Lihong Niu · Lou Sun · Lu Liu

Received: 9 December 2008 / Accepted: 5 June 2009 / Published online: 20 June 2009
© Springer Science + Business Media, LLC 2009

Abstract The absorption, fluorescence, and transient absorption spectra of Tetra(α -amino) zinc phthalocyanine, $\text{ZnPc}(\alpha\text{-NH}_2)_4$, have been measured in polar solvents and compared with that of $\text{ZnPc}(\alpha\text{-R})_4$ ($\text{R}=\text{H}$, NO_2 , $\text{OCH}(\text{CH}_3)_2$). While the latter three showed the typical photophysics of phthalocyanines, $\text{ZnPc}(\alpha\text{-NH}_2)_4$ exhibits distinct spectral properties, a very low fluorescence quantum yield and a relatively long fluorescence lifetime. These observations are explained by the substantial charge transfer characters in the absorption and fluorescence spectra of $\text{ZnPc}(\alpha\text{-NH}_2)_4$. NMR indicates that intramolecular H-bonding makes atoms in NH_2 actually coplanar with other elements of $\text{ZnPc}(\alpha\text{-NH}_2)_4$. The local excited state is non emissive and the weak emission is assigned to its charge transfer state. The transient absorption bands from laser flash photolysis located at 630 nm, 645 nm is assigned to the mono-charge transfer state, while that at 545 nm is assigned to the di-charge transfer state.

Keywords Amino phthalocyanine · Fluorescence · Photophysics · Synthesis · Charge transfer

Introduction

Amino phthalocyanines have been tested as red-region fluorescence probes [1–5], organic electro-luminescent materials [6–8], synergic photosensitizers [9], and photo-

catalytic oxidants [10]. The photophysical properties, especially fluorescence and triplet parameters, are among the major controlling factors for these applications. The related study on amino substituted phthalocyanines is still rare in sharp contrast with that of other commonly substituted phthalocyanines, which have been reviewed in several reports [11–14]. In our previous reports the photophysical behavior of halogenated and sulfonated phthalocyanines were explored [15–17]. We now extend the study to amino phthalocyanines. The peripheral introduction of amino groups into a phthalocyanine may show some remarkable different effects from that of other substituents, because an amino group may concurrently play several roles as: a good electron donor, a strong proton acceptor, a hydrogen-bonding participant, and a good ligand of metal ions. For example, its strong electron-releasing ability makes amino phthalocyanines suitable as excellent electron donors in photoinduced electron transfer [18]. During this study, the title compound was found to show a very low fluorescence quantum yield and distinct spectral properties different from other substituted phthalocyanines, while the fluorescence lifetime does not decrease significantly. The purpose of this investigation is to examine its photophysical properties in detail and try to understand the results by comparison with other regular phthalocyanines $\text{ZnPc}(\alpha\text{-R})_4$ with the structures as shown in Scheme 1 ($\text{R}=\text{OCH}(\text{CH}_3)_2$, H , NO_2 , NH_2).

The abbreviations and the meaning of symbols for physical quantities are given in Table 1.

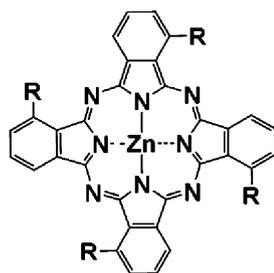
X.-F. Zhang (✉) · X. Li · L. Sun · L. Liu
Department of Chemistry,
Hebei Normal University of Science and Technology,
Qinghuangdao, Hebei Province, PR China 066004
e-mail: zhangxianfu@tsinghua.org.cn

L. Niu
Chemistry Department, Tsinghua University,
Beijing, PR China 100084

Experimental section

Materials

All organic solvents were dried by appropriate methods and distilled before use. ZnPc was purchased from Tokyo Kaise.



ZnPc(α-R)₄

R = H, NO₂, OCH(CH₃)₂, NH₂

Scheme 1 Chemical structure of phthalocyanines (ⁱPr=isopropyl)

ZnPc(α-NO₂)₄, ZnPc(α-OⁱPr)₄, H₂Pc(β-NH₂)₄ and ZnPc(β-NH₂)₄ were synthesized and reported before [16]. All other reagents were of analytical grade and used as received.

Characterization

¹H NMR spectra were recorded at room temperature on a Bruker dmx 300 MHz NMR spectrometer. MS spectra were recorded on a Bruker APEX II and a Micromass GCT-MS spectrometer. Samples for C, H, N elemental analysis were dried under vacuum, and analyzed with a Carlo Erba-1106 instrument.

Synthesis of substituted zinc phthalocyanines

The route used to prepare ZnPc(α-NH₂)₄ and the ZnPc(α-NO₂)₄ is based on previous work [16].

ZnPc(α-NO₂)₄ A mixture of 1.93 g (10 mmol) 3-nitrophthalic anhydride, 0.55 g (25 mmol) ZnAc₂•2H₂O, 10 g urea and 0.01 g ammonium molybdate was finely ground and placed in a 250 ml beaker. The beaker in an oil bath was heated to 160 °C and stirred until no bubbles were observable. After cooling down, 100 ml 1.0 M HCl was added to the resulting solid and boiled with stirring for 1 h. After filtrating the mixture and washing it with deionized water to pH neutral, the solid was treated with 1.0 M NaOH similarly. The acid-base treatment was repeated three times, the solid was then dried and weighted to be 1.2 g (63%). For characterization, please see Table 2.

ZnPc(α-NH₂)₄ Finely ground ZnPc(α-NO₂)₄ (5 g, 6.38 mmol) was reduced with an aqueous solution of sodium sulfide nanohydrate (25 g, 104 mmol) at 50°C for 5 h to its corresponding amino derivative. Yield: 3.4 g (80%). For characterization, please see Table 2.

ZnPc(β-NH₂)₄ The same procedure was applied as that of ZnPc(α-NH₂)₄ except ZnPc(α-NO₂)₄ was replaced by

ZnPc(β-NO₂)₄. Yield: 2.95 g (70%). For characterization, please see Table 2.

H₂Pc(β-NH₂)₄ The same procedure was applied as that of ZnPc(β-NH₂)₄ except ZnPc(β-NO₂)₄ was replaced by H₂Pc(β-NO₂)₄. Yield: 2.61 g (61%). For characterization, please see Table 2.

Photophysical measurements

DMF and other solvents were dried and freshly distilled before use. Measurements were carried out at room temperature of 22 °C. UV/Vis (ultraviolet/visible) absorption measurements were made with a HP 8451A spectrophotometer in 10 mm quartz cuvettes. Fluorescence spectra were monitored at wavelengths up to 900 nm using a Perkin Elmer LS 55. The slit width was chosen to match a wavelength band of 10 nm. All spectra were corrected for the sensitivity of the photo-multiplier tube. The fluorescence quantum yields (Φ_f) were calculated by Φ_f = F_sA₀Φ_f⁰/(F₀A_s), in which F represents fluorescence intensity expressed by the integral of a spectrum, A is the absorbance at excitation wavelength, the subscript s stands for a sample while subscript (or superscript) 0 indicates reference standard. Samples were measured relative to ZnPc in DMF (Φ_f⁰ = 0.30) [19]. Excitation wavelengths of 610 nm corresponding to S₀ to S₁ transitions were employed. The sample and reference solutions were

Table 1 Abbreviations and symbols for physical quantities

CT	charge transfer
DMF	N,N-dimethylformide
DMSO	dimethylsulfoxide
H ₂ Pc	metal free phthalocyanine
ICT	intramolecular charge transfer
ⁱ Pr	isopropyl
LE	local excited state
Pc	phthalocyanine
S ₀	ground state
S ₁	lowest excited singlet state
TICT	twisted intramolecular charge transfer
UV/Vis	ultraviolet/visible
ZnPc	Zinc phthalocyanine
Physical quantities for absorption and fluorescence spectra:	
A	Absorbance
F	Fluorescence Intensity
Φ _f	fluorescence quantum yield
τ _f	fluorescence lifetime
λ _{em}	emission wavelength
λ _{ex}	excitation wavelength

Table 2 Characterization data for the prepared compounds

	Elemental analysis, % ^S Required (Found)	IR, cm ⁻¹	MS, m/Z	¹ H NMR*
ZnPc(α -NO ₂) ₄	C 50.7 (50.8), H 1.6 (1.8), N 22.2 (22.4)	ν (NO ₂): 1538.2, 1352.1	757.9 (M+1)	n.d. [#]
ZnPc(α -NH ₂) ₄ ·2H ₂ O	C 57.8 (57.9), H, 3.6 (3.8), N 24.8 (25.0), Zn 9.4 (9.7)	ν (NH ₂): 3324.8, 3420.3	638.2 (M+1)	See a) ^{&}
ZnPc(β -NH ₂) ₄ ·2H ₂ O	C 57.8 (57.3), H, 3.6 (3.8), N 24.8 (24.4), Zn 9.4 (9.0)	ν (NH ₂): 3351.1, 3426.7	638.2 (M+1)	See b) ^S
H ₂ Pc(β -NH ₂) ₄	C 66.9 (66.3), H 3.9 (4.2), N 29.3 (28.9)	ν (NH ₂): 3205.2, 3294.1	575.2 (M+1)	n.d. [#]

S: relative error is $\pm 0.3\%$. *: 300MHZ, DMSO-d₆; #: not determined owing to solubility; a)[&] δ 8.60 (*m*, 4H, Ar-H), δ 7.91(*s*, 4H, Ar-H), δ 7.67(*s*, 4H, Ar-H), δ 7.47(*s*, 4H, NH), δ 7.27(*s*, 4H, NH); b)^S δ 8.91 (*m*, 4H, Ar-H), δ 8.41 (*d*, 4H, Ar-H), δ 7.35 (*d*, 4H, Ar-H), δ 6.25 (*s*, 8H, NH₂). The meaning of symbols for NMR spectrum: Ar-H for Aromatic hydrogen, δ for chemical shift, *d* for doublet, *m* for multiplet, *s* for singlet, *t* for triplet.

prepared with the same absorbance (A_i) at the excitation wavelength (near 0.09 per cm). All solutions were air saturated. Fluorescence lifetime of S_1 was measured by time-correlated single photon counting method (Edinburgh FL-900 spectrophotometer) with excitation at 660 nm by a portable diode laser (Edinburgh Instruments). Longer accumulation time for emission signals are employed to measure the lifetimes of amino phthalocyanines.

Transient spectra were recorded with an Edinburgh LP-920 laser flash photolysis system, oxygen in samples were removed by bubbling N₂ for 15 min in DMF before measurements. A Nd:YAG laser (Continuum surelite II, 355 nm and 7 ns FWHM, repetition rate of 10 Hz) was used as excitation source. The analyzing light was from a xenon lamp. The laser and analyzing light beams perpendicularly passed through a quartz cell with an optical path length of 1 cm. The signal was displayed and recorded on a Tektronix TDS 3012B oscilloscope and an Edinburgh LP900 detector. The laser energy incident at the sample was attenuated to a few mJ per pulse. Time profiles at a series of wavelengths from which point-by-point spectra were assembled were recorded with the aid of a PC controlled kinetic absorption spectrometer. The concentrations of the target compounds were typically 10 μ M providing $A_{355}=0.2$ in a 10 mm cuvette.

Results and discussion

The absorption, emission and excitation spectra of ZnPc(α -NH₂)₄ are shown in Fig. 1, and the related photophysical properties are summarized in Table 3. ZnPc(α -NH₂)₄ features a much lower fluorescence quantum yield (Φ_f) 0.0011 than 0.30 of ZnPc, while its fluorescence decay contains two components of 1.80 ns (68%) and 8.30 ns (32%), for which even the short lifetime (τ_f) is not reduced too much from 3.69 ns of ZnPc. To understand this result, two other phthalocyanines ZnPc(α -R)₄ with typical electron-donating R=OⁱPr (isopropoxy) or electron-withdrawing R=NO₂, are also included for comparisons. The UV/Vis

absorption, steady state and kinetic fluorescence emission, and transient absorption were recorded in polar solvents since ZnPc(α -NH₂)₄ is not soluble in nonpolar or low polarity solvents.

The electronic absorption spectra of four phthalocyanines in DMF are shown in Fig. 2. Differences between the spectrum of ZnPc(α -NH₂)₄ with that of the other three ordinary phthalocyanines are obvious. Compared to ZnPc, the red shift of absorption maximum for ZnPc(α -NH₂)₄ is 95 nm, which is much larger than 24 nm for ZnPc(α -OⁱPr)₄ and 1 nm for ZnPc(α -NO₂)₄. Also noted is the more remarkable broadening of the Q band for ZnPc(α -NH₂)₄ than any other phthalocyanines (the band width at half height is 18 nm, 18 nm, 22 nm and 54 nm for R=H, NO₂,

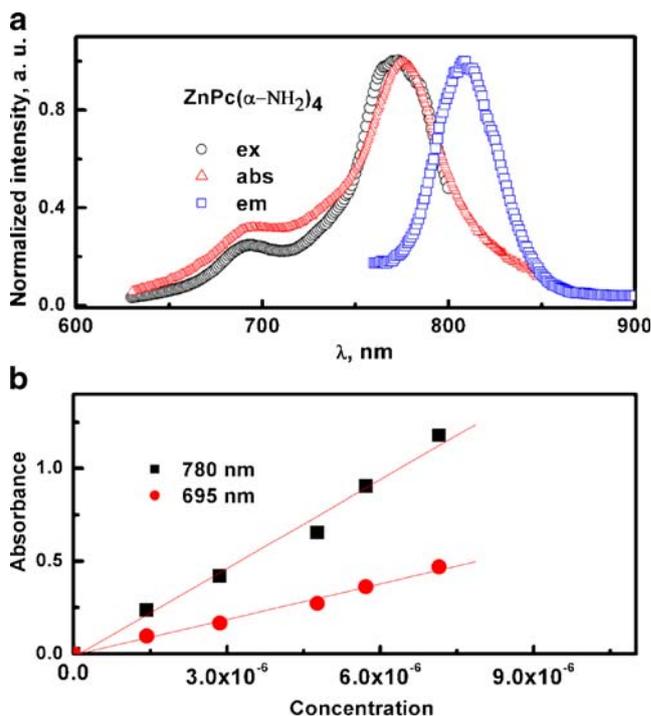


Fig. 1 **a** The normalized spectra of absorption, emission (λ_{em} : 610 nm) and excitation (λ_{em} : 860 nm) for ZnPc(α -NH₂)₄ in DMSO (6.1 μ M). **b** It shows the linear dependence of absorbance on its concentration

Table 3 Photophysical parameters for ZnPc(R)₄ in DMF*

	λ_{abs} , nm	λ_{em} , nm	ϵ , $10^5 \text{ M}^{-1} \text{ cm}^{-1}$	Φ_f	τ_f , ns
ZnPc	670	681	2.75	0.30	3.69±0.037
ZnPc(α -NO ₂) ₄	671	683	1.41	0.23	2.73±0.043
ZnPc(α -O ⁱ Pr) ₄	702	724	1.71	0.22	3.01±0.052
ZnPc(α -NH ₂) ₄	765	790	1.56	0.0011	1.96±0.04(74%), 9.24±1.24(26%)
ZnPc(β -NH ₂) ₄	725	756	–	0.0043	2.49±0.062(75%), 10.90±2.33(25%)
H ₂ Pc(β -NH ₂) ₄	715	774	–	0.0120	1.73±0.061(61%), 6.34±0.66(39%)

*: λ_{abs} is absorption maximum. λ_{em} is emission maximum. ϵ is molar absorption coefficient. Φ_f is fluorescence quantum yield, relative error ca. 10%. τ_f is fluorescence lifetime.

OⁱPr and NH₂, respectively). A new band for ZnPc(α -NH₂)₄ appears at 485 nm, which is weak and very broad but not occurred in the spectrum of ZnPc. This 485 nm absorption cannot be attributed to impurity since the excitation of this band also generates the same fluorescence as that produced by excitation at Q band absorptions. The presence of both the widened Q band and the new broad 485 nm absorption are indications of the involvement of substantial charge transfer character.

With the addition of a few drops of trifluoroacetic acid to protonate the nitrogen atoms of four amino groups, the 485 nm band of ZnPc(α -NH₂)₄ gradually disappeared while the 765 nm Q band was blue shifted back to the normal shape of ZnPc. This titration effect suggests that the occurrence of 485 nm band and the widened Q band of ZnPc(α -NH₂)₄ are directly related to the lone-pair electrons on amino groups. Ouedraogo [20] and Dale [21] also observed the similar band between 400 nm and 550 nm in the absorption spectra of metal phthalocyanine derivatives with axial nitrogen ligands, which was assigned to charge transfer transition (CT) from the ligands to aromatic phthalocyanine ring rather than to metal ion. By analogy, we may also assign the 485 nm band

to be CT from amino groups to the phthalocyanine ring of ZnPc(α -NH₂)₄, in which CT is even made easier because of the direct linkage between them.

In the cases of Ouedraogo [20] and Dale [21], CT transition in the Q band region was not observed which was believed resulting from the fact that the first CT transition is forbidden ($b_{2g} \rightarrow e_g$ or $e_g \rightarrow e_g$). In our case of ZnPc(α -NH₂)₄, however, the first CT transition is partially allowed which is evidenced by i) the remarkable widening of the Q band shown previously, and ii) the much larger dependence of the Q band location of ZnPc(α -NH₂)₄ on solvent polarity than that of ZnPc. For example, the absorption maxima of ZnPc(α -NH₂)₄ in four solvents with increasing polarity are red shifted 33 nm from 743 nm in acetone to 751 nm in methanol, 763 nm in DMF and 776 nm in DMSO; while the corresponding values for ZnPc are 665 nm, 666 nm, 670 nm and 672 nm, respectively, which changed only 7 nm. Fluorescence spectra of ZnPc(α -NH₂)₄ in these solvents showed the same tendency.

The UV/Vis absorption of the metal-free amino substituted phthalocyanine showed similar behavior as that of ZnPc(α -NH₂)₄ [16], which provides another evidence that the origin of the CT band is not related to central metal but a transition from ligand to π system of the phthalocyanine.

Figure 3 shows the normalized fluorescence spectra for the phthalocyanines. The introduction of nitro groups into zinc phthalocyanine presents little effect on the emission spectrum. The emission band of ZnPc(α -NH₂)₄, however, is much broader and more red-shifted than that of any other phthalocyanines. Also noted is the absence of vibrational structure in the fluorescence of ZnPc(α -NH₂)₄ which violates the mirror-image symmetry between excitation and emission spectra, as depicted in Fig. 1. The broadness and structurelessness of the fluorescence of ZnPc(α -NH₂)₄ are consistent with the typical features of charge transfer emission. The emission maximum of ZnPc(α -NH₂)₄ in acetone, methanol, DMF and DMSO is 776 nm, 778 nm, 790 nm, and 808 nm, respectively, which shows much larger dependency on solvent polarity than that of the ZnPc which changed only a few nano meters.

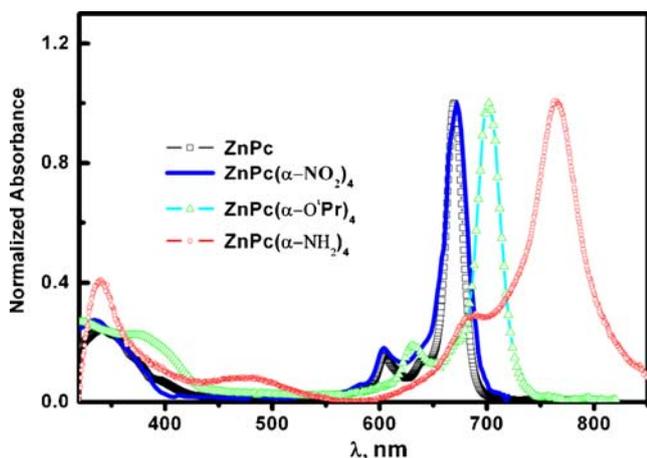


Fig. 2 The UV-Vis absorption spectra in DMF for ZnPc (3.57 μM), ZnPc(α -NO₂)₄ (7.14 μM), ZnPc(α -OⁱPr)₄ (5.88 μM), ZnPc(α -NH₂)₄ (6.39 μM)

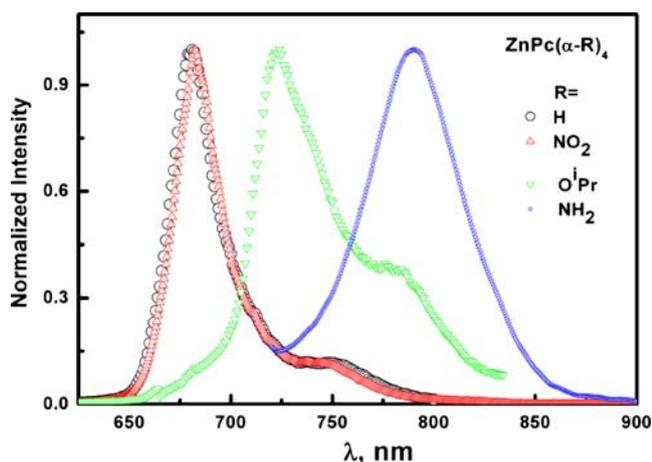


Fig. 3 The normalized fluorescence spectra in DMF for ZnPc, ZnPc(α -NO₂)₄, ZnPc(α -OⁱPr)₄, ZnPc(α -NH₂)₄. The excitation wavelength is 610 nm for ZnPc, ZnPc(α -NO₂)₄, ZnPc(α -OⁱPr)₄, and 700 nm for ZnPc(α -NH₂)₄. In each case, the absorbance at the respective wavelength was adjusted to be less than 0.09

The Φ_f of all three substituted ZnPcs are decreased compared to that of ZnPc, but the Φ_f of ZnPc(α -NH₂)₄ shows much more intense reduction than the other two. The variation of τ_f for ZnPc(α -NH₂)₄, on the other hand, does not show the same trends as its Φ_f .

The decay traces for fluorescence of ZnPc, ZnPc(α -NO₂)₄ and ZnPc(α -OⁱPr)₄ can be well fit by monoexponential function with τ_f of 3.69 ns, 2.73 ns and 3.34 ns respectively as shown in Fig. 4. But the emission decay of ZnPc(α -NH₂)₄ is biexponential, in which the major component has a short τ_f of 1.8 ns (68%) and the minor one has a long τ_f of 8.0 ns (32%). By using ZnPc as a reference, the percentage decrease of τ_f for each of ZnPc(α -NO₂)₄ and ZnPc(α -OⁱPr)₄ is comparable to the reduction of

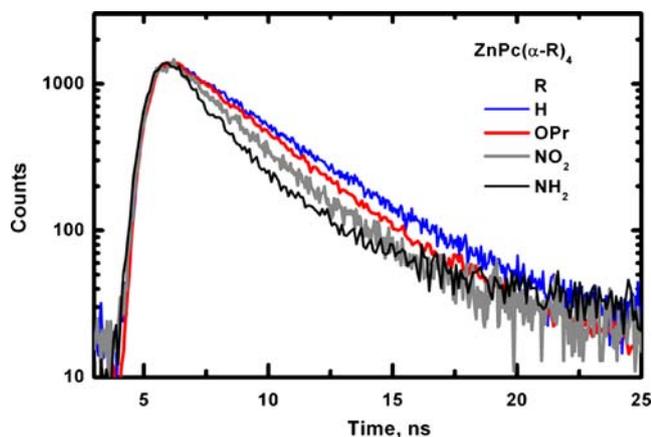


Fig. 4 The emission decay traces in DMF for ZnPc, ZnPc(α -NO₂)₄, ZnPc(α -OⁱPr)₄, ZnPc(α -NH₂)₄. The excitation wavelength is 660 nm of a diode laser with the pulse width <100 ps, absorbances at the wavelength were adjusted to be 0.10

its Φ_f . This is not the case for ZnPc(α -NH₂)₄, the τ_f of its short component is dropped down to 50% of that of ZnPc, while its Φ_f is only 0.37% of that of ZnPc. We therefore conjecture that the observed emission of ZnPc(α -NH₂)₄ originates from its intramolecular charge transfer state (ICT) rather than its local excited state (LE) as illustrated in Fig. 6. Such charge transfer emission and absorption spectra have been observed for quite some amino substituted aromatic hydrocarbons in which dual fluorescence could occur in some cases owing to the TICT (twisted intramolecular charge transfer) [22–25]. Amino groups have also been shown to be able to transfer electrons to ZnPc [26]. By using H₂N-NH₂ as a reducing agent, the excitation of phthalocyanines by irradiation > 500 nm was reported to generate the aromatic monoanion of ZnPc [26]. In our case of this study, there are four NH₂ groups directly linked to ZnPc, and will be equally motivated to transfer electron charge to the same excited state of ZnPc when photoexcited, it is therefore even easier to form CT state than the intermolecular case of H₂N-NH₂.

In the high polar solvents of this study that strongly favor the charge transfer, the fluorescence from the local excited state is very likely fully quenched and the τ_f became too short to be measured. It is therefore not surprising that only the charge transfer emission could be recorded.

Phthalocyanines may form H-type aggregate that is not emissive [15]. In the case of ZnPc(α -NH₂)₄, a linear relation between absorbance and its concentration is obeyed as shown in Fig. 1b. Its excitation spectrum also coincides with its absorption as shown in Fig. 1. We can therefore exclude the possibility of the effect of aggregation that can lower the Φ_f of ZnPc(α -NH₂)₄.

NMR of ZnPc(α -NH₂)₄ is shown in Fig. 5. The most notable is the splitting of the two hydrogen atoms on amino

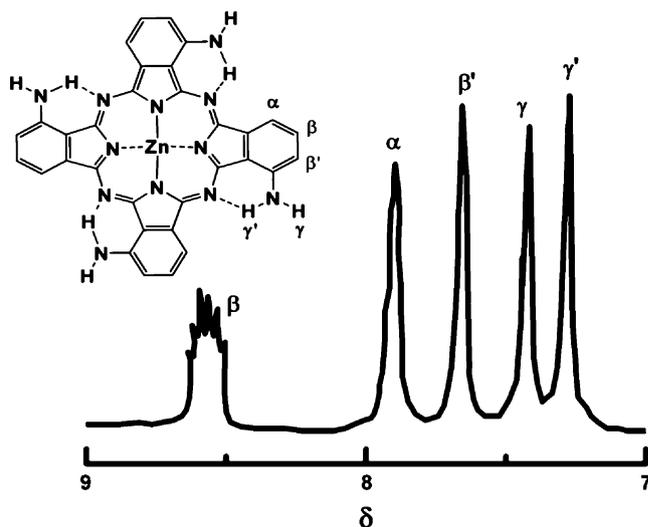


Fig. 5 The NMR of ZnPc(α -NH₂)₄ in DMSO-d₆

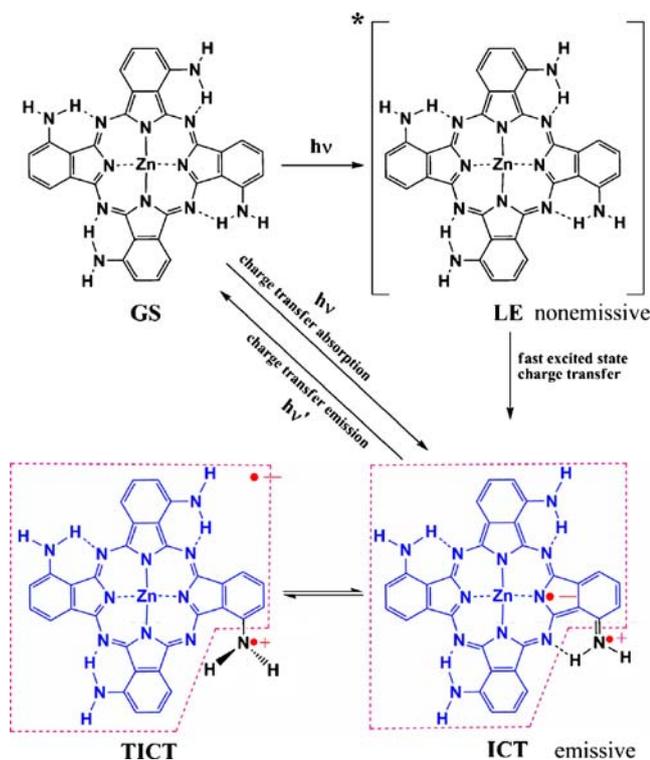


Fig. 6 Emission ($h\nu'$) from single-charge separated state of $\text{ZnPc}(\alpha\text{-NH}_2)_4$. GS: ground state, LE: local excited state, ICT: intramolecular charge transfer, TICT: twisted intramolecular charge transfer. In TICT, the positive-charged N is not conjugated with the large π system, while in ICT it is. The dashed frame indicates the delocalization range of the negative charge

group, which is obviously caused by the H-bonding formation as shown in Fig. 5. Such a H-bond is stabilized by the formation of a six-membered cycle and makes H atoms in NH_2 coplanar with the aromatic ring of $\text{ZnPc}(\alpha\text{-NH}_2)_4$. The presence of H-bond suppresses the free rotation of NH_2 along the C-N bond and favors the charge transfer from the lone electrons in the vertical π orbital of N to the aromatic ring, in particular when it is photoexcited.

Based on the analysis above, we tentatively give the emission mechanism for $\text{ZnPc}(\alpha\text{-NH}_2)_4$ in Fig. 6. The presence of TICT is also concluded below according to the observation from transient absorptions. The double exponential decay of the observed emission reflects the two ICT state before and after solvent stabilization, respectively.

$\text{ZnPc}(\alpha\text{-NH}_2)_4$ can be viewed as a strongly coupled donor-acceptor system in which four amino groups are the donor subunits while the aromatic core of zinc phthalocyanine is the acceptor. If photo excitation induces charge transfer, the anion formed should appear in the transient absorption measurements. We therefore compared the laser flash photolysis results of ZnPc and $\text{ZnPc}(\alpha\text{-NH}_2)_4$. The assignment of transients photogenerated in $\text{ZnPc}(\alpha\text{-NH}_2)_4$ can be fulfilled by comparing with the absorption spectra recorded in the photoreduction of ZnPc by $\text{H}_2\text{N-NH}_2$ [26].

Figure 7 shows the transient absorption spectra of ZnPc and $\text{ZnPc}(\alpha\text{-NH}_2)_4$ in degassed DMF upon laser excitation at 355 nm. ZnPc (Fig. 7a) showed the typical spectrum of PC compounds, i.e. a broad band centered at 480 nm, attributed to the $T_1 \rightarrow T_n$ triplet absorption together with the photo-bleaching of the ground state [27, 28]. Fitting the decay curve at absorption maximum generated the triplet lifetime to be 180 μs , agrees well with the data in literature [28].

For $\text{ZnPc}(\alpha\text{-NH}_2)_4$ in Fig. 7b, the broad band of $T_1 \rightarrow T_n$ triplet-triplet absorption did not occur, attributed to the fact that S_1 is quenched by fast charge transfer and thus the formation of its triplet state by intersystem crossing is inhibited. The transient absorption maximum instead occurs at 630 nm, together with a close shoulder at 645 nm and another peak at 545 nm. The 630 and 645 nm bands can be assigned to the monoanion $[\text{ZnPc}(\alpha\text{-NH}_2)_3]^{-(\text{NH}_2)^+}$, which is similar but slightly red-shifted to the reported absorption spectrum of $[\text{ZnPc}]^{-(\text{H}_2\text{N-NH}_2)^+}$ at the positions [29, 30]. In the absence of oxygen the transient decay measured at

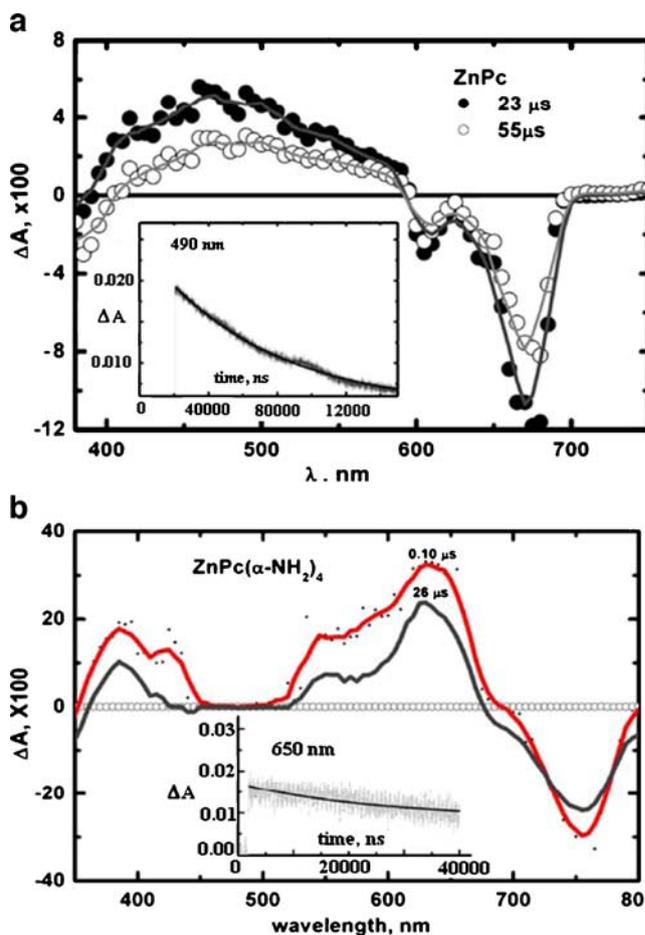


Fig. 7 Transient absorptions of ZnPc (a) and $\text{ZnPc}(\alpha\text{-NH}_2)_4$ (b) in argon saturated DMF with laser excitation at 355 nm, the absorbance at 355 nm was adjusted to be 0.2. Inset shows the decay of absorbance at a particular wavelength

645 nm was well fit by the biexponential function and gave pretty long lifetimes of 63.7 μs and 31.4 μs , respectively. In air saturated DMF, the two lifetimes are reduced to 56.6 and 23.9 μs , respectively. The quenching rate constant by oxygen is therefore estimated to be in the order of 10^6s^{-1} , which is very inefficient and further rules out the possibility of the transient signal to be $T_1 \rightarrow T_n$ triplet-triplet absorption.

Comparing with the reported absorption spectra for the photoreduced ZnPc by $\text{H}_2\text{N-NH}_2$ [26], the 545 nm band is very similar to that of dianion $[\text{ZnPc}]^{2-} \cdots (\text{H}_2\text{N-NH}_2)^{2+}$ which was generated by exciting ZnPc to its S_2 state with 330 nm irradiation. In our case of laser irradiation at 355 nm, S_2 population of $\text{ZnPc}(\alpha\text{-NH}_2)_4$ is easier, together with the fact that four NH_2 are directly attached to ZnPc, the formation of dianion $[\text{ZnPc}(\alpha\text{-NH}_2)_2]^{2-}[(\text{NH}_2)^+]_2$ will show even higher possibility, except for an expected red shift of the peak position.

The absorption maximum of mono-charge separated state, i.e. $[\text{ZnPc}(\alpha\text{-NH}_2)_3]^{-(\text{NH}_2)^+}$, shows a 110 nm blue shift from that of $\text{ZnPc}(\alpha\text{-NH}_2)_4$. While the absorption of the dianion $[\text{ZnPc}(\alpha\text{-NH}_2)_2]^{2-}[(\text{NH}_2)^+]_2$ presents a further 100 nm blue shift. Both remarkable blue shifts indicate that the $(\text{NH}_2)^+$ in $[\text{ZnPc}(\alpha\text{-NH}_2)_3]^{-(\text{NH}_2)^+}$ is rotated away from the planar position and causes the breaking of H-bond and the shrinking of π conjugation system. This is an evidence for the presence of TICT in Fig. 6. In other words, the transient bands at 630, 645 nm and 545 nm are owing to the absorptions of TICT state. The transient absorption of ICT state, on the other hand, cannot be observed because its lifetimes of 1.8 and 8.3 ns are beyond the detection range limited by the laser pulse width of 7 ns.

The observed emission around 780 nm is from the ICT state in Fig. 6 rather than TICT state based on the match between the excitation and absorption spectra in Fig. 1.

Conclusion

The photophysical properties of $\text{ZnPc}(\alpha\text{-NH}_2)_4$ have been measured and compared with that of $\text{ZnPc}(\alpha\text{-R})_4$ ($\text{R}=\text{H}$, NO_2 , O^iPr). While the latter three showed the typical photophysics of phthalocyanines, both the absorption and emission spectra of $\text{ZnPc}(\alpha\text{-NH}_2)_4$ exhibits substantial charge transfer characters. Intramolecular H-bonding makes atoms in NH_2 actually coplanar with other atoms of $\text{ZnPc}(\alpha\text{-NH}_2)_4$. The local excited state of the $\text{ZnPc}(\alpha\text{-NH}_2)_4$ is nonemissive in polar solvents. The observed weak emission around 780 nm is originated from the coplanar charge transfer state rather than TICT state. By comparing with the findings in the photoreduction of ZnPc by $\text{H}_2\text{N-NH}_2$, the transient absorptions from laser flash photolysis located at 630 nm, 645 nm can be assigned to the monoanion, while that at 545 nm is assigned to the dianion.

Acknowledgements We thank HBUST and the Key Laboratory of Photochemistry, Chinese Academy of Sciences for financial support.

References

- Gómez-Hens A, Aguilar-Caballos MP (2004) Long-wavelength fluorophores new trends in their analytical use. *Trends Analyt Chem* 23:127–136. doi:10.1016/S0165-9936(04)00305-X
- Chen XL, Li ZB, Zhu YX, Xu JG (2004) Sensitive fluorimetric method for the determination of aniline by using tetra-substituted amino aluminium phthalocyanine. *Anal Chim Acta* 505:283–287. doi:10.1016/j.aca.2003.10.067
- Chen XL, Yang HH, Zhu QZ, Zheng H, Xu JG, Li DH (2001) A new red-region substrate, tetra-substituted amino aluminium phthalocyanine, for the fluorimetric determination of H_2O_2 catalyzed by mimetic peroxidases. *Analyst (Lond.)* 126:523–527. doi:10.1039/b009253n
- Zhan XQ, Li DH, Zhu QZ, Xu JG, Zheng H (2000) Sensitive fluorimetric determination of formaldehyde by the co-quenching effect of formaldehyde and sulfite on the fluorescence of tetra-substituted amino aluminium phthalocyanine. *Analyst (Lond.)* 125:2330–2334. doi:10.1039/b005432j
- Chen XL, Li DH, Yang HH, Zhu QZ, Zheng H, Xu JG (2001) Study of tetra-substituted amino aluminum phthalocyanine as a new red-region substrate for the fluorometric determination of peroxidase and hydrogen peroxide. *Anal Chim Acta* 434:51–58. doi:10.1016/S0003-2670(01)00819-4
- Mortimer RJ, Dyer AL, Reynolds JR (2006) Electrochromic organic and polymeric materials for display applications. *Displays* 27:2–18. doi:10.1016/j.displa.2005.03.003
- Jung SH, Choi JH, Yang SM, Cho WJ, Ha CS (2001) Syntheses and characterization of soluble phthalocyanine derivatives for organic electroluminescent devices. *Mater Sci Eng B* 85:160–164. doi:10.1016/S0921-5107(01)00600-6
- Mortimer RJ (1999) Organic electrochromic materials. *Electrochim Acta* 44:2971–2981. doi:10.1016/S0013-4686(99)00046-8
- Lunardi CN, Tedesco AC (2005) Synergic photosensitizers: a new trend in photodynamic therapy. *Curr Org Chem* 9:813–821. doi:10.2174/1385272053764944
- WenXing C, ShiLiang C, ShenShui L, YuYuan YAO, MinHong XU (2007) Photocatalytic oxidation of phenol in aqueous solutions with oxygen catalyzed by supported metallophthalocyanine catalyst. *Sci China, Ser Biol Chem* 50:379–384
- Ishil K, Kobayashi N (2003) The photophysical properties of phthalocyanines and related compounds. In: Kadish KM, Smith KM, Guillard R (eds) *The porphyrin handbook*. Academic Press, San Diego, pp 1–42
- Nyokong T (2007) Effects of substituents on the photochemical and photophysical properties of main group metal phthalocyanines. *Coord Chem Rev* 251:1707–1722. doi:10.1016/j.ccr.2006.11.011
- Tedesco AC, Rotta JCG, Lunardi CN (2003) Synthesis, photophysical and photochemical aspects of phthalocyanines for photodynamic therapy. *Curr Org Chem* 7:187–196. doi:10.2174/1385272033373076
- Ferraudi G (1989) Photochemical properties of metallophthalocyanines in homogeneous solution. In: Leznoff CC, Lever ABP (eds) *Phthalocyanines: properties and applications*. VCH, New York
- Zhang X-F, Xu H (1993) Influence of halogenation and aggregation on photosensitizing properties of zinc phthalocyanine (ZnPc). *J Chem Soc, Faraday Trans* 89:3347–3351. doi:10.1039/ft9938903347
- Zhang X-F, Xu H (1994) Synthesis and photophysical properties of substituted zinc phthalocyanines. *Chem Res Chin Univ* 15: 917–921

17. Zhang X-F, Ma J, Xu H (1993) Photophysical properties of some water soluble metal phthalocyanines. *Proc. SPIE* 1616:372–375. doi:10.1117/12.137035
18. Zhang X-F, Cui X, Liu Q, Zhang F (2008) Multiple-charge separation in nanoscale artificial photosynthetic models. *Chem-PhysChem* 9:1514–1518. doi:10.1002/cphc.200800191
19. Seybold PG, Gouterman M (1969) Porphyrins XIII: fluorescence spectra and quantum yields. *J Mol Spectrosc* 31:1–13. doi:10.1016/0022-2852(69)90335-X
20. Ouedraogo GV, More C, Richard Y, Benlian D (1981) Charge-transfer and Moessbauer spectra of axially substituted iron phthalocyanines. *Inorg Chem* 20:4387–4393. doi:10.1021/ic50226a069
21. Dale BW (1969) Effect of axial ligands upon the electronic absorption spectrum of phthalocyanineiron(II). *Trans Faraday Soc* 65:331–339. doi:10.1039/tf9696500331
22. Chen H, Jiang Y-B (2000) Photophysics of 1-dimethylaminonaphthalene in aqueous-organic binary solvents. *Chem Phys Lett* 325:605–609. doi:10.1016/S0009-2614(00)00741-7
23. Barik A, Kumbhakar M, Nath S, Pal H (2005) Evidence for the TICT mediated nonradiative deexcitation process for the excited coumarin-1 dye in high polarity protic solvents. *Chem Phys* 315:277–285. doi:10.1016/j.chemphys.2005.04.018
24. Inokuma Y, Easwaramoorthi S, Yoon ZS, Kim D, Osuka A (2008) meso-(4-(N, N-Dialkylamino)phenyl)-substituted subporphyrins: remarkably perturbed absorption spectra and enhanced fluorescence by intramolecular charge transfer interactions. *J Am Chem Soc* 130:12234–12235. doi:10.1021/ja804846v
25. Druzhinin SI, Bursulaya BD, Uzhinov BM (1995) Planar and twisted intramolecular charge transfer states of the excited proton transfer products of aminocoumarins. *J Photochem Photobiol A* 90:53–56
26. Maslov VG, Sidorov AN (1974) The photochemical generation of negative phthalocyanine and porphyrin ions. *Theor Exp Chem* 7:680–683. doi:10.1007/BF00524988
27. Ishil K, Kobayashi N (2003) The photophysical properties of phthalocyanines and related compounds. In: Kadish KM, Smith KM, Guillard R (eds) *The porphyrin handbook*. Academic Press, San Diego, pp 1–42
28. Bishop SM, Beeby A, Parker AW, Foley DPMS (1995) The preparation and photophysical measurements of perdeutero zinc phthalocyanine. *J Photochem Photobiol A* 90:39–44
29. Mack J, Stillman MJ (2001) Assignment of the optical spectrum of metal porphyrin and phthalocyanine radical anions. *J Porphyrins Phthalocyanines* 5:67–71. doi:10.1002/1099-1409(200101)5:1<67::AID-JPP300>3.0.CO;2-3
30. Mack J, Kobayashi N, Stillman MJ (2006) Magnetic circular dichroism spectroscopy and TD-DFT calculations of metal phthalocyanine anion and cation radical species. *J Porphyrins Phthalocyanines* 10:1219